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Composite films of lead zirconate titanate (PZT)/poly vinylidene fluoride (PVDF), PZT/Copolymer of vinylidene fluoride - trifluorethylene (VDF-TrFE) and Barium titanate ($BaTiO_3$)/PVDF were prepared in our laboratories and their electrical, dielectric and pyro-electric properties were investigated. PZT phase appears to provide a significant contribution to the electrical conductivity of these composites whereas the dielectric dispersion is influenced by the polymer and copolymer phase. The composite film of PZT/VDF-TrFE appears to be an attractive electro-active material with a pyroelectric coefficient an order of magnitude greater than that of PVDF whereas its figure of merit is significantly higher than that of PZT.

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071

Introduction

Composite films containing ferroelectric ceramic inclusions in the matrix of suitable polymers may possess high dielectric constants with good electrical breakdown strength and enhanced piezo- and pyroelectric coefficients. Such composite materials will have commercial applications as high energy storage capacitor and piezo- and pyro-electric sensors including medical uses. It has been our objective to prepare and study the electro-active properties of such composite films with suitable ceramics such as lead zirconate titanate (PZT) embedded in the matrix of polymers such as polyvinylidene fluoride (PVDF), copolymers of vinylidene fluoride and trifluorethylene (VDF-TrFE). The following is an account of the work performed in our laboratories. There have been six publications with the results of this work and copies of these (reference item 4 - 8 and 15) are included in this report.

2. Sample Preparation

Several types of Polymer/ceramic composites have been prepared by mixing PZT powder with an average grain size of 20μm with different polymers using a rolling mill operated at 433k. The composite hides were then pressed in a temperature-controlled hydraulic press to thickness in the range 100 - 800μm. The use of high quality chromium plates for pressing allowed the production of films with a good surface structure. Samples were then thoroughly cleaned with isopropyl alcohol in an ultrasonic bath to remove surface contaminants and thus improve repeatability of data obtained with dielectric and electrical measurements. The following five different types of composites have been prepared with different volume fractions of the two phases.

Table 1:

	Materials	Designation
(i)	PZT5/PVDF (50:50 Vol%)	Composite A
(ii)	PZT8/PVDF (50:50 Vol%)	Composite B
(iii)	PZT5/VDF - TrFE (50.50 Vol%)	Composite C
(iv)	PZT8/VDF - TrFE (50:50 Vol%)	Composite D
(v)	$BaTio_3$/PVDF (40:60 Vol%)	Composite E

PZT and $BaTio_3$ powder with an average grain size of 20μm were purchased from Unilator Technical Ceramics of Ruabon U.K. Pellets of PVDF (solef 1008) and VDF-TrFe (Solef 11010) were kindly supplied by Laporte Industries of Luton, U.K. Electroactive properties of four composite films, together with those of Piezel (see Appendix for specification), a commercially available composite of PZT/VDF-TrFE, manufactured by the Daikin Industry Limited of Japan have been studied in the present work. These studies include (i) dielectric properties in the frequency range 10^{-4}Hz to 10^{5}kHz (ii) absorption and desorption currents up to 10^{5} seconds after application and removal of poling voltages up to $10^{7}Vm^{-1}$ in the temperature range of 293 - 378K, (iii) thermally stimulated discharge current (TSDC) and (iv) the pyroelectric behaviour in the temperature range of 293 - 378K.

3. Experimental

Aluminium electrodes of area 2cm x 2cm were vacuum deposited on both sides of each composite film. The samples were then thermally treated in an evacuated measurement chamber at a pressure of 10^{-6} torr at 373K with their electrodes shorted for at least 12 hours before any dielectric and electrical measurements were made.

The dielectric dispersion measurements were made using a General Radio Bridge (type 1621) or with a system comprising of a Solartron frequency response analyser and BBC microcomputers which have been recently developed in our laboratories.

The absorption current and TSDC measurements were made in a stainless steel vacuum chamber ($<10^{-6}$ torr). Temperature was controlled to within 0.25K using a Eurotherm controller. A high voltage was applied to samples from a Brandenburg photomultiplier supply and the currents were measured with a Keithley (model 616) digital electrometer suitably interfaced to a microcomputer which stored data, performed transformations on line and plotted curves.

The pyroelectric currents were measured using a direct method [1] by applying a linear heating rate of approximately 1^{0}c per minute to the samples which have been poled appropriately. The pyro- electric current responses were also studied by a dynamic method [2,3] by exposing the samples to a well-focussed radiation from a tungsten filament lamp.

4. Results & Discussion

Although six different types of composites (Composites A - E and Piezel) have been studied in this work, the most interesting composites are possibly samples A, B, C, D and Piezel. PZT 5 materials (composite A and C) are donor doped with niobium, compensation being achieved by electrons or cation vacancies. These defects lead to higher domain wall mobility and greater dielectric losses. The electro-active properties of composite A and C were observed to be similar and to avoid duplication this report will include only the results obtained with the Composite C.

PZT 8 materials (composite B and D) are acceptor doped with iron which results in oxygen vacancies to compensate for the charge deficiency. It is believed that these vacancies associate with the domain walls within the grains, thus effectively pinning them. Thus reduction of mobility is the cause for the lower dielectric losses in PZT 8. Once again the electro-active properties of the composites B and D were observed to be similar and the report will not include the results obtained with the composite D. The electro-active behaviour of the remaining composite E ($BaTiO_3$/PVDF) appears to be less attractive in comparison with PZT based composites (prepared in our laboratories) as may be observed from the attached publication [reference 15].

4.1 Dielectric Behaviour

Figure 1 shows the behaviour of the real and imaginary parts (ε^1 and ε^{11}) of the complex dielectric constants [5] of the composite samples B (PZT8/PVDF) and C (PZT5/VDF - TrFE) and Piezel in the frequency range of 10 Hz to 10^5Hz. It may be observed that in the high frequency region the values of ε^1 are about the same for all three composites. However, at low frequencies the ε^1 values are significantly different. According to Yamada et al [9] the permittivity ε, for a composite system is given by

$$\varepsilon = \varepsilon_1 \left[1 + \frac{nq\ (\varepsilon_2 - \varepsilon_1)}{n\varepsilon_1 + (\varepsilon_2 - \varepsilon_1)\ (1 - q)} \right] \qquad (1)$$

where n is a parameter attributed to the shape of the ellipsoidal ceramic particles, q the volume fraction of the ceramic particles, ε_1 the permittivity of the continuous polymer (host) phase and ε_2 the permittivity of the ellipsoidal ceramic particles. Taking the value of ε_1 (PVDF) = 11, ε_2 = 1240 (PZT) and the value of n chosen as 8 to fit equation 2, the calculated values of the relative permittivity ε_1 at 1 kHz are 20 for 10% vol. PZT and 90 for 50% volume fraction of PZT. These calculated values are in reasonable agreement with the experimentally observed values (figure 1). The dielectric loss (ε^{11}) behaviour shows a broad peak in the region 10^3 - 10^4 Hz which may be due to the relaxation of the polymer phase which occurs at similar frequencies and temperature region.

The dielectric loss is seen to increase considerably at low frequencies particularly for higher content of PZT in PZT/PVDF [7] indicating the dominance of PZT at low frequencies.

Figure 2 shows the dielectric loss behaviour [7] against temperature in the composite of PZT/PVDF and Piezel. The observed peaks which occur at ~ 360K in PZT/PVDF and at ~ 350K in Piezel are due to a relaxation which is associated with molecular motions in the crystalline region of the polymer. The observed behaviour (figure 2) of ε^{11} also demonstrates the substantial contribution of the interfacial effect of the polymer-ceramic composite materials at high temperatures.

4.2 <u>Absorption Current Studies</u>

The time dependence of charging currents in PZT/Polymer composites [5] are shown in figure 3. It may be observed that in all cases the currents decrease monotonically with time following the well known expression

$$I(t) = A(T)\ t^{-n} \qquad (2)$$

where A is a temperature dependent factor, t the time after application (or removal) of the external voltage and $n \lesssim 1$. For the upper two curves the behaviour of I(t) is similar for the two composites which were prepared using different types of PZT and different polymer grades of equal volume percentage between the ceramic and polymer phases. The current in piezel samples was observed to reach a steady state level at $\sim 10^5$s whereas in the composites B and C, the time taken to obtain a steady state conduction level was observed to be shorter. The analysis of the study state current in the composition for different temperature and fields [7,8] (see figure 4) show that its behaviour is governed by an ionic hopping mechanism with a substantial contribution from the PZT phase at high temperatures. Assuming a model of diffusion of lattice defects or ions and a carrier hopping process [10] the following expression is obtainable for a steady state current I_s for low fields.

$$I_s = I_o \exp\ (-\mu/kt)\ \mathrm{Sinh}\ (\frac{edf}{2kt}) \qquad (3)$$

when I_o is a constant, μ the activation energy, E the electric field, of the jump distance and the other symbols have their usual meanings. Equation 3 reduces to

$$I_s = I_o \exp\ (^{-\mu}/_{kt})\ \exp\ (^{edE}/_{2kt}) \qquad (4)$$

which is similar to an expression derived by Lawson [11] for the high field dependence. From the ionic conduction plots, obtained in this work (see figure 3) the value of jump distance d, and the activation energy E, for the composite were observed to be 90nm and 0.8eV respectively [7]. These values are similar to those of PZT [7], thus suggesting that the origin of the steady state conduction is of ionic nature in both materials and that the role of PZT is dominant in the conduction process for the composites. A comparison of data for 10% and 50% volume fraction of PZT shows that as the content of PZT phase is increased, the magnitude of jump distance (d-value) increases.

4.3 Thermally Stimulated Discharge Current (TSDC) Studies

TSDC analysis of polymer solids provides quantitative information of bulk polarization and qualitative information of molecular motion and anisotrophy of microstructure. The thermoelectric schedule of a TSDC analysis is as follows (see figure 5). A polarizing electric field is applied across the sample at an elevated temperature. The material is then cooled to a suitable low temperature in the presence of the field. The external field is then removed. The sample now possesses an electrical 'frozen-in' persistent polarization. The electrodes of the sample are then shorted and the material is heated at a slow uniform rate (~10^{o}/minute). As the temperature rises, the induced persistent polarization begins to decay, and whenever a temperature range is encountered over which the decay rate matches the time scale of the experiment, there follows a release of some of these charges. A plot of this current as a function of temperature is a TSDC thermogram.

A TSDC analysis obeys the following expression:

$$\omega = A/bkT_m^2 \tag{5}$$

where ω is the test frequency, A the apparent activation energy, b the inverse heating rate, k the Boltzmann's constant and T_m the temperature at which TSDC reaches its maximum. Figure 6 shows [12] typical TSDC spectra of corona poled PVDF from which it can be seen that increasing the polarizing voltage increases the magnitude of the current released. Both curves display a broad peak at ~49^{o}c and have similar profiles.

A typical pattern [7] of TSDC spectra of PZT5/VDF-TrFE with 50:50 Vol % is shown in figure 7. The sample was poled in air at a field of 1.2×10^{7} Vm^{-1} at 373K for 2.8 hours and then cooled to room temperature in the presence of the field. It was then placed in a vacuum measurement chamber for TSDC measurement The first run shows a very high increase in current with no peak up to 373k. From the shape of the curve it may be possible to observe a peak if it was heated above 373K. A similar observation has also been made by Shakhtakhtinski et al [13] in which no peak has been observed below 373K for a composite of PZT/polyethylene. The second TSDC run shows a substantial reduction of current as some space charges have been released during the first heating (TSDC) run. The third subsequent heating shows no appreciable reduction of current, thus establishing a truly pyroelectric current of dipolar origin. This latter point is further discussed in the next section.

4.4 Pyroelectric Behaviour

The pyroelectric behaviour of the composites have been investigated in the work both by the direct method [1] and by the dynamic method [2,3] as mentioned earlier. In the direct method [1] which is probably the more accurate of the two, the pyroelectric current I_p is related to the pyroelectric coefficient p(T) thus,

$$I_p = a\, p\,(T)\, \frac{dT}{dt} \tag{6}$$

a is the electroded sample area and dT/dt the rate of change of temperature. It should be noted that I_p is the short circuited current measured at a uniform heating rate. Thus the reversible pyroelectric coefficient can be directly determined from the TSDC runs, mentioned in the previous section provided the trapped space charges have been eliminated with several TSDC runs.

The pyroelectric coefficients as a function of temperature, obtained by the direct method [1] for the composites B (PZT8/PVDF), C (PZT5/VDF - TrFE) and piezel are shown in figure 8 from which [5] it may be observed that the sample B with the highest dielectric loss (see figure 1) has the lowest pyroelectric coefficient at low temperatures, whereas sample C and piezel appear to have similar p(T) values. Factors such as elastic stiffness, thermal expansion of the polymer and internal stresses may contribute significantly to the observed differences in p(T) values of the present results in the same manner as the result of Galgoci et al [14] showed.

The dynamic method [2,3] provides an alternative way in measuring the pyroelectric response of materials. The pyroelectric coefficient p(T) in this method may be obtained from the following relation [2].

$$I_{p(max)} = Bp(T) \tag{7}$$

$$\text{with } B = \frac{F_o a}{\rho C_p L} \vartheta^{\frac{\vartheta}{1 - \vartheta}} \tag{8}$$

where $I_{p(max)}$ is the peak value of the pyroelectric response when a thermal radiation is incident on the surface of a sample with shorted electrodes, ρ the density of the material, F_o the radiation power absorbed per unit area of the electroded sample, C_p the specific heat of the sample material of thickness L, a the electroded area of the sample and $\vartheta = Ce/C_{th}$ where Ce and C_{th} are the electrical and thermal time constants of the system respectively.

In this work I_p (max) has been measured after the completion of the third TSDC run of the prepoled sample in order to establish the true reversibility of the pyroelectric response. Figure 9 shows the behaviour of the pyroelectric current peak $I_{p(max)}$ obtained by the dynamic method as a function of the poling fields [5] at 333K and 373K. It may be observed that the data show an approximately linear relationship at the respective temperatures and within the range of fields employed in this work.

Now $I_{p(max)}$ measured with the dynamic method, must be related to the p(T) values obtained by the direct method. Figure 10 shows a plot [5] of $I_{p(max)}$ dynamic method/p(T), direct method for the Sample C at 333K. This relationship appears to be linear, as expected, and is expressed thus,

$$I_{p(max)} = Gp(T) \quad (9)$$

where $G = 2.1 \times 10^{-5}\ m^2\ s^{-1}K$ which may be considered as a constant for the same sample material with the same electrode geometry for the same incident power of radiation. The thermal and electrical time constant of the system, of course, remain unchanged.

An efficient poling is obviously achieved at high temperatures, fields and at long poling time. Care should, however be exercised that the material does not suffer an electrical breakdown. The results of a study of these three poling parameters, i.e. the poling field E_p, temperature T_p and time t_p with respect to the induced pyroelectricity, have been summarised in figure 11 for the composite C (PZT5/VDF-TrFE, 50:50 vol%). It may be observed that a pyroelectric coefficient of ~ $14 \times 10^{-5}\ C\ m^{-2}K^{-1}$ can be obtained for the composite C with $E_p = 1 \times 10^7\ Vm^{-1}$ T_p = 373K and t_p = 8 hours with thermal poling.

Finally Table 2 summarises the results of the present studies of the electrical, dielectric and pyroelectric properties of all the materials which have been investigated in our laboratories including the composites B, C and E and piezel. It is evident from these results that the pyroelectric coefficient p(T) of composite C is about an order of magnitude greater than those of the homopolymer PVDF and piezel. The figure of merit $(p(T)/\varepsilon^1)$ of the composite C is also higher than those of PZT, PVDF and piezel by the same amount.

Conclusion

It has been possible to produce mechanically strong films of ceramic copolymer composite (PZT5/VDF-TrFE, 50:50 vol%) which are significantly better than piezel with respect to their pyroelectric properties. Composite C is thus an attractive and marketable sensor material which may have considerable advantage in industrial, defence and bio-medical application. This project has produced new useful material with desirable electro-active properties.

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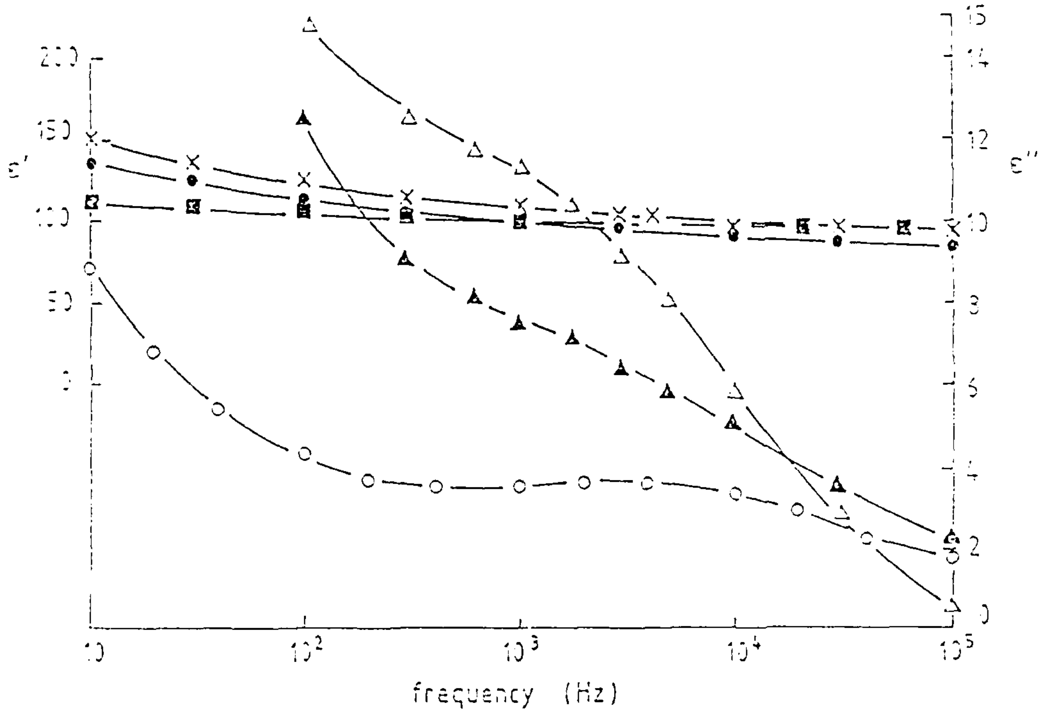

Fig. 1 : The behaviour of ε' and ε'' against frequency in Composites B and C and PIEZEL at 363 K.
PZT8/PVDF (B) 50/50 : ε' (x), ε'' (Δ)
PZT5/VDF-TrFE (C) 50/50 : ε' (●), ε''(▲)
PIEZEL : ε' (■), ε''(○)

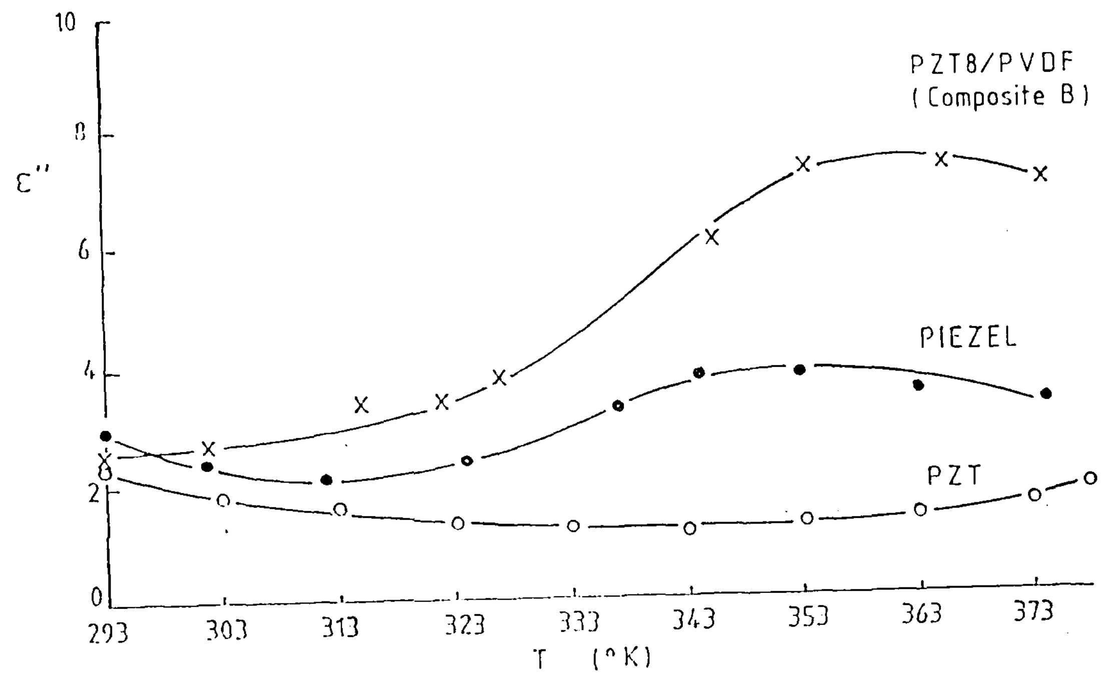

Figure 2 : Dielectric loss behaviour against temperature in PZT , Composite B and PIEZEL at 1 kHz.

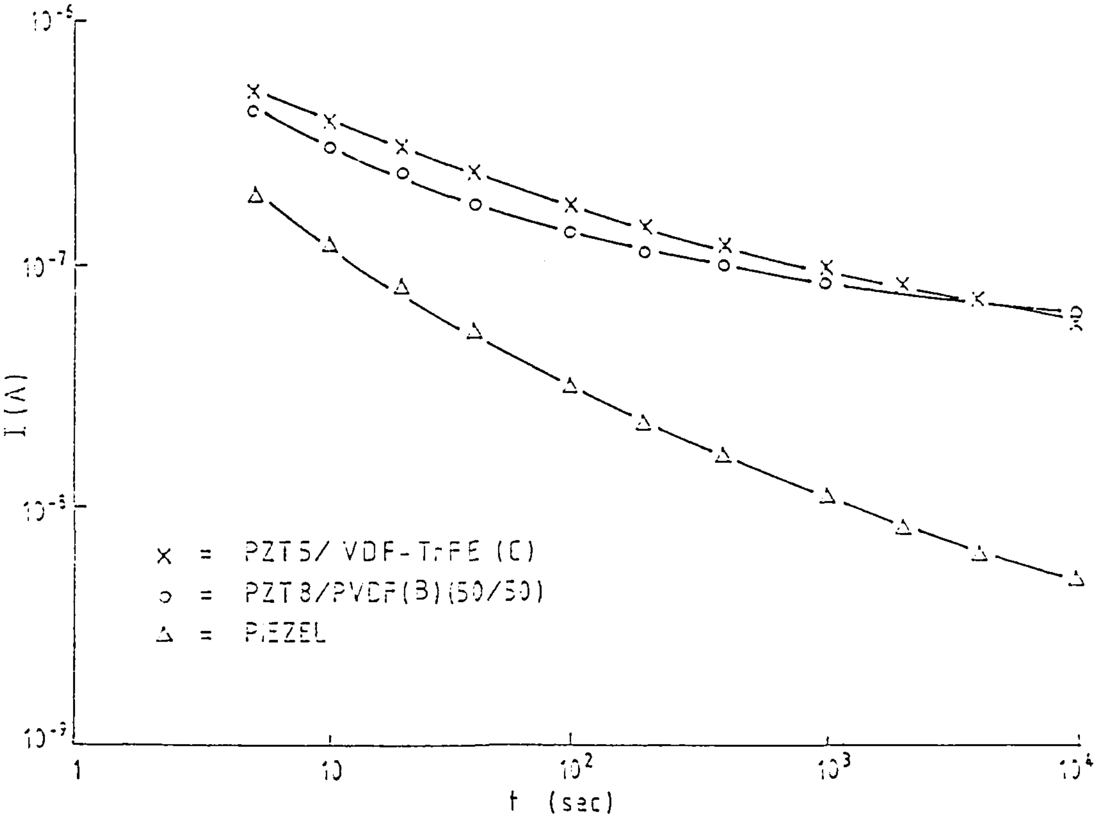

Fig. 3 : Charging currents in Composites B and C and PIEZEL at 363 K and field $1.75 \times 10^6\ Vm^{-1}$.

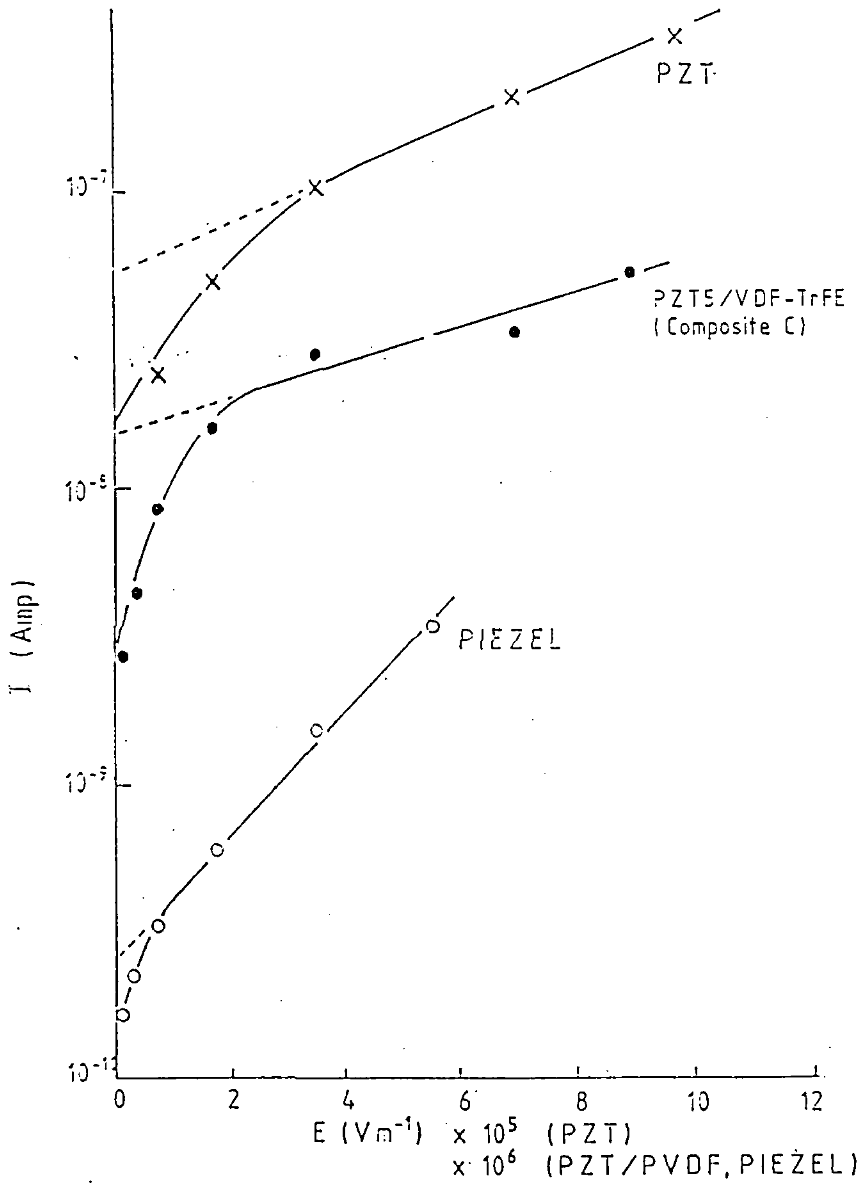

Figure 4: Isochronal charging currents at 10^4 sec as a function of field in PZT, Composite C and PIEZEL at 343K.

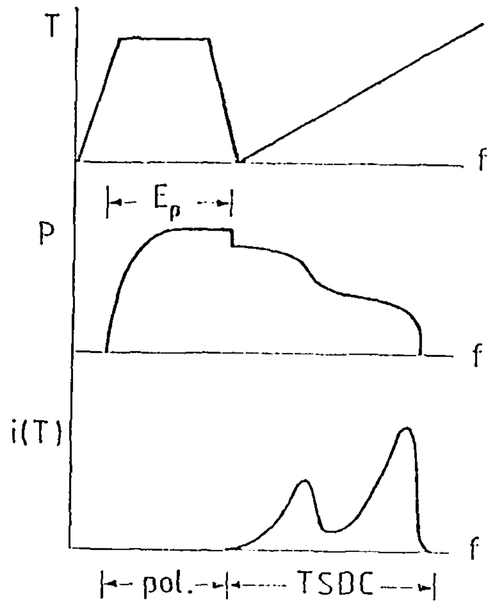

Figure 5:
Sequence of events during a TSDC experiment. The temperature schedule followed is shown at the top. The first stage (pol.) involves application of external voltage E_v across the specimen at an elevated temperature, and the second stage, TSDC, involves measurement of the current flowing between the short-circuited electrodes as the specimen is heated at a constant rate. In the example depicted here, the polarization P developed during the polarizing stage is shown to decay arbitrarily in two stages and, as a direct consequence, a peak in discharge current i(T) is seen coincident with each decay process.

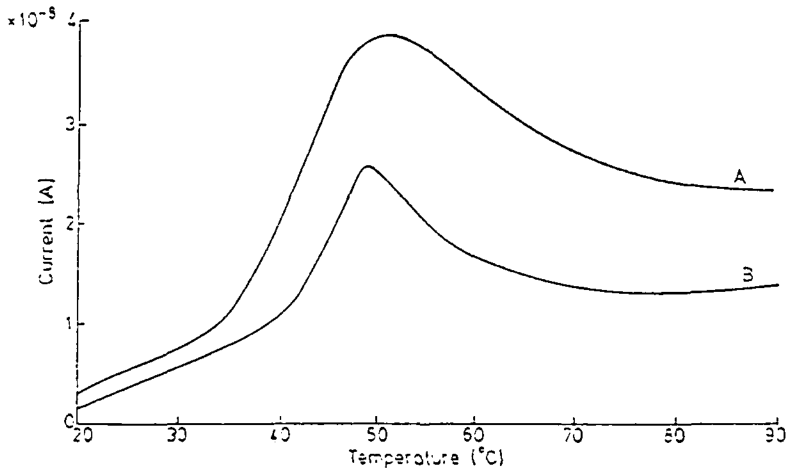

Figure 6: Thermally stimulated current (TSC) during the first heating cycle (irreversible) in corona charged PVF_2 film of 25 μm thickness: A, Corona potential 10 kV, charging time 100 s and charging temperature 20 °C; B, Corona potential 5 kV, otherwise as in A.

Material : PVDF.

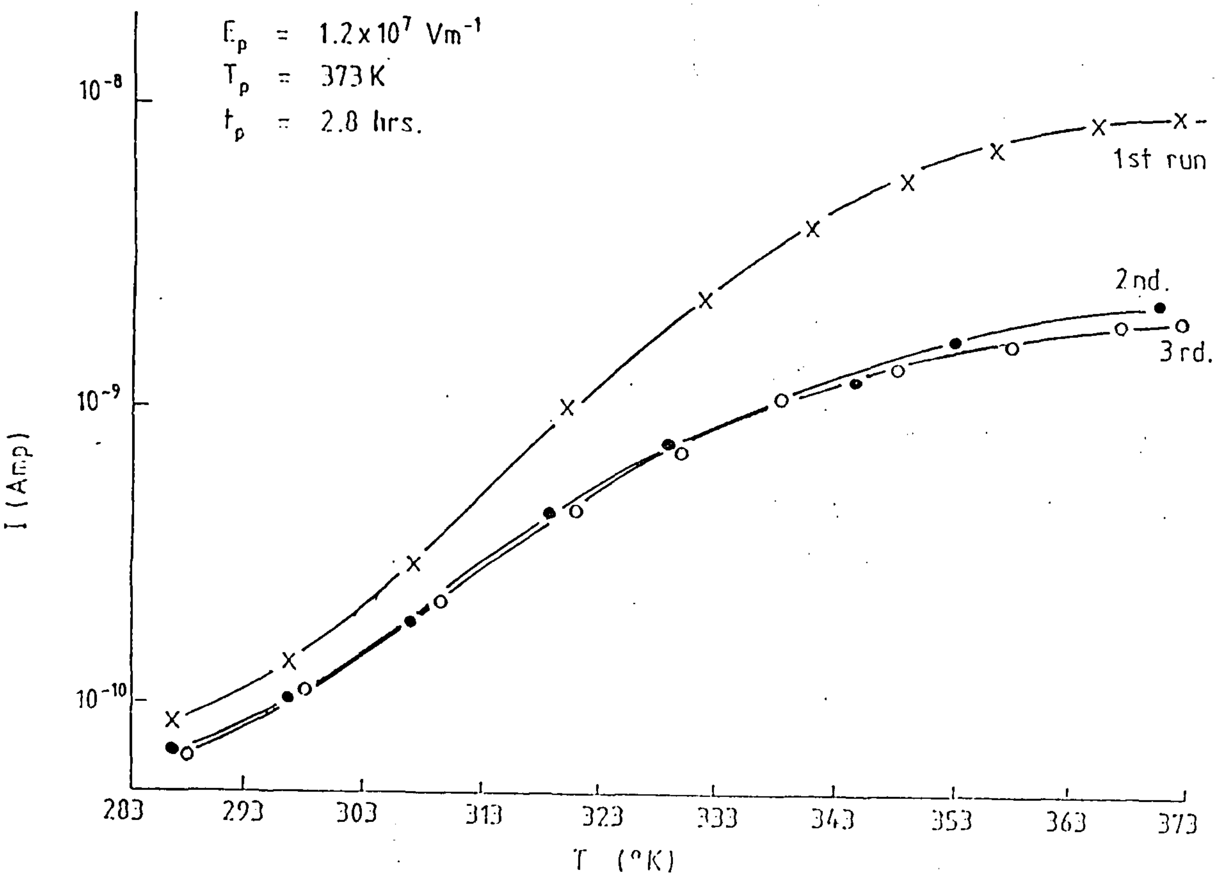

Figure 7 . Typical thermally stimulated discharge current and pyroelectric current in PZT5/VDF-TrFE (composite)C).

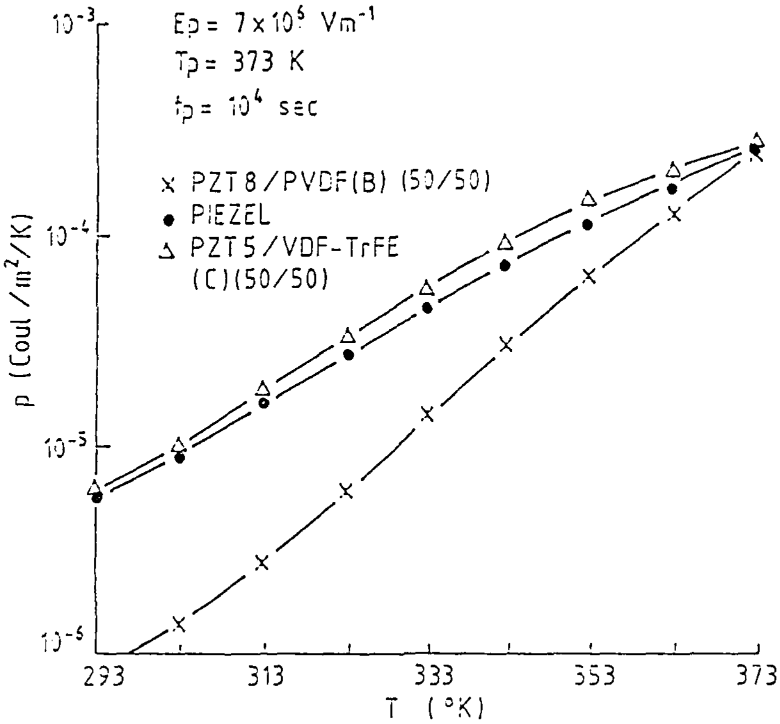

Fig. 8 : Pyroelectric coefficient against temperature in Composites B & C and PIEZEL.

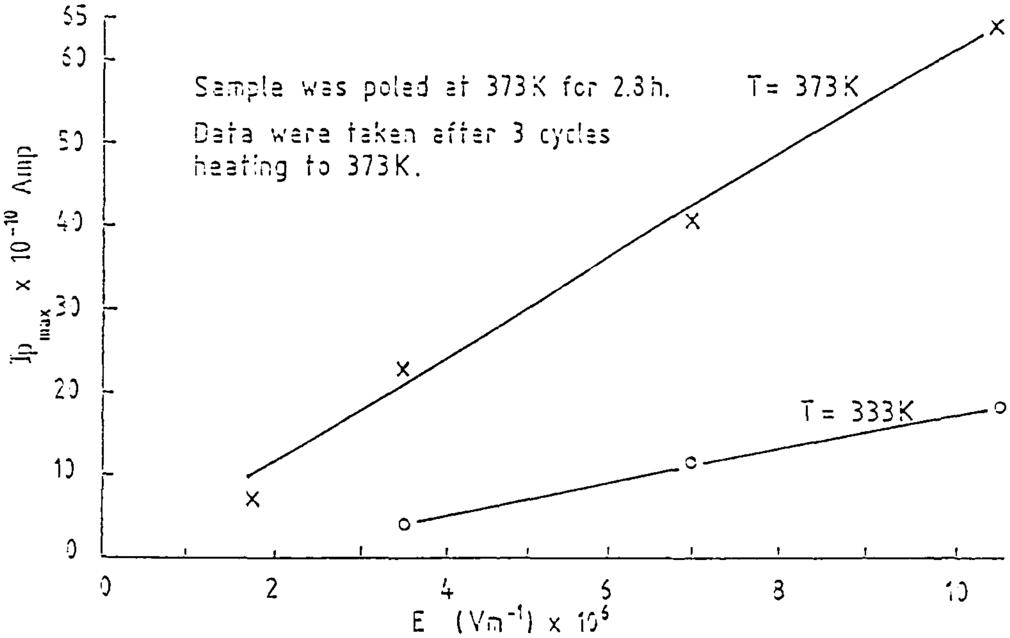

Fig. 9 : Peak current against poling field in PZT5/VDF-TrFE (Composite C).

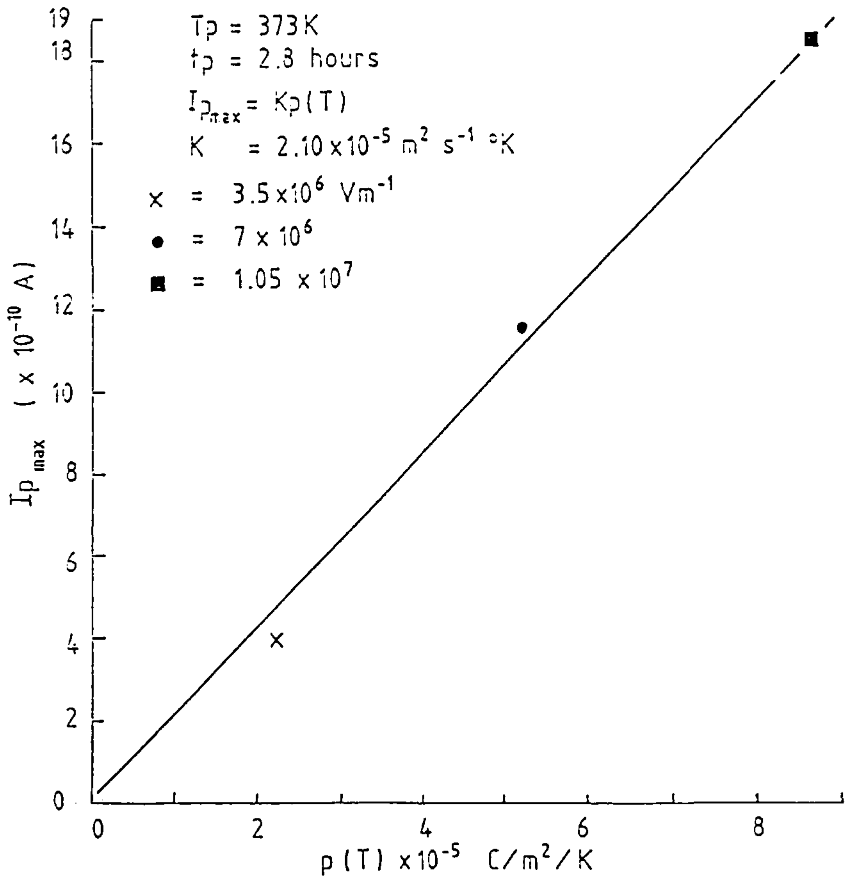

Fig. 10 : Peak current against pyroelectric coefficient at 333K in PZT5 / VDF-TrFE (Composite C)

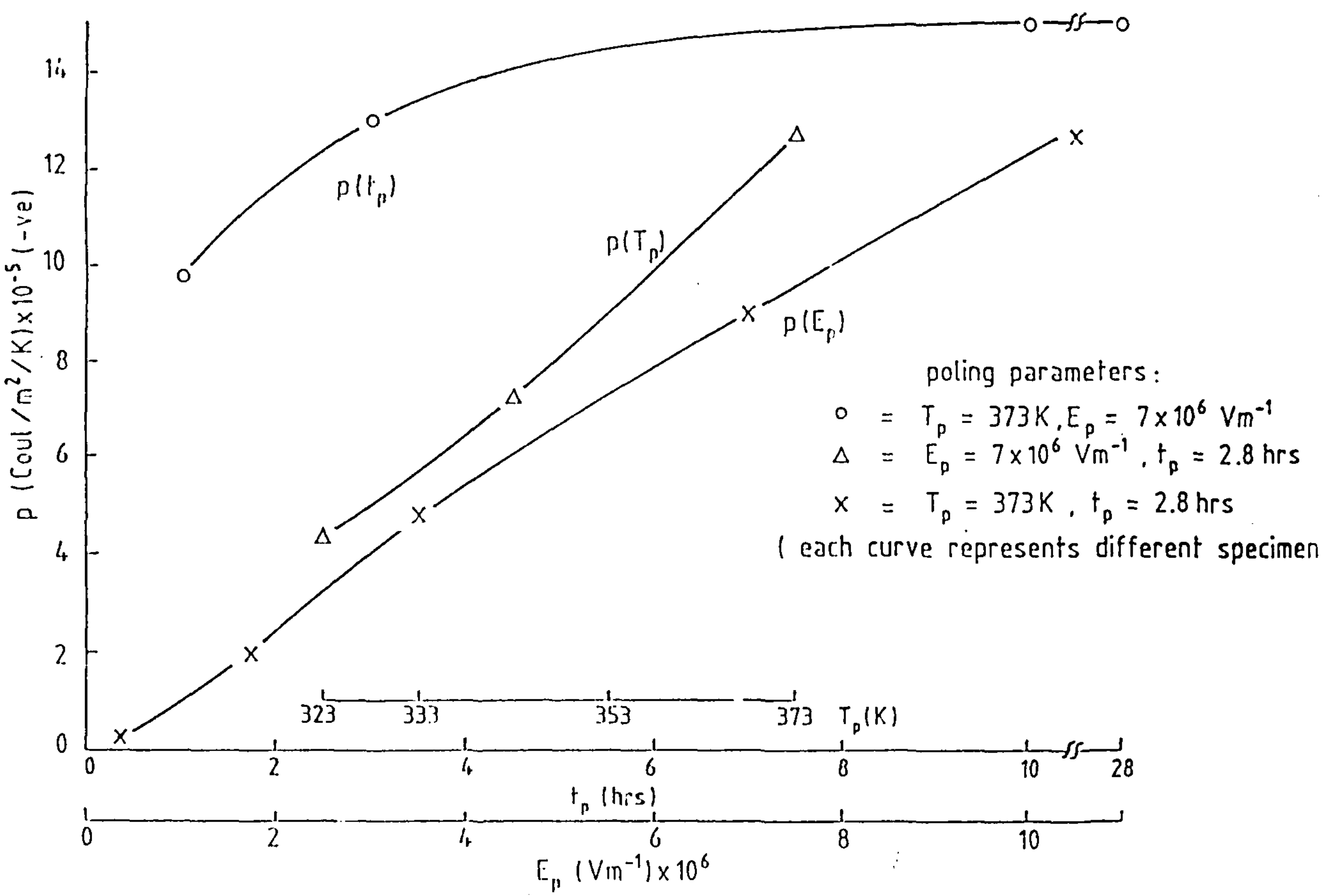

Figure 11 . The dependence of pyroelectric coefficient on poling parameters at 343 K in PZT8/VDF-TrFE (Composite C)

TABLE 2. SUMMARY OF RESULTS

	$\sigma(\Omega^{-1}m^{-1})$ (90°C)	ϵ' (70°C) (1KHz)	ϵ'' (70°C) (1kHz)	Pyrelectric Coefficient p(T) $(Coul.m^{-2}K^{-1})$ (70°C)	Pyroelectric Figure of Merit p/ϵ' (70°C)
PZT	$3x10^{-9}$	1300	1.2	$5x10^{-4}$	$3.8x10^{-7}$
$BaTiO_3$	$10^{-9}-10^{-8}$	1700		$7x10^{-4}$	$4.1x10^{-7}$
PVDF	$3x10^{-13}$	12	1.0	$9.0x10^{-6}$	$7.5x10^{-7}$
Composite C [PZT5/VDF-TrFE] 50:50	$1.4x10^{-10}$	95	6.0	$1.4x10^{-4}$	$1.5x10^{-6}$
Composite B [PZT8/PVDF] 50:50	$1.3x10^{-10}$	96	6.5	$3.3x10^{-5}$	$3.4x10^{-7}$
Composite E [$BaTiO_3$/PVDF] 40:60	$3x10^{-10}$	73	6.2	$8.0x10^{-6}$	$1.1x10^{-7}$
Piezel (Daikin Industries, Japan)	2×10^{-10}	12	0.95	9.0×10^{-6}	7.5×10^{-7}

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DIELECTRIC AND PYROELECTRIC PROPERTIES OF POLYMER-CERAMIC COMPOSITE

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Abstract The dielectric and the pyroelectric behaviour and the nature of absorption and steady state of currents have been studied for a ceramic and a polymer-ceramic composite over wide ranges of frequency and poling field and a limited range of temperature. The relative permittivity and the pyroelectric coefficient of the composite are observed to be significantly higher than those of the polymer. The dielectric loss processes of the composite are observed to be dominated by those of the polymer whereas the ceramic phase contributes significantly to the steady state electrical conduction which is observed to be of ionic nature.

1. INTRODUCTION

Ferroelectric ceramics exhibit high permittivity, piezo and pyroelectric effects and are, therefore, useful materials for diverse applications, viz. high energy storage capacitors, optical switching devices, vidicon targets, acoustic emission detection, medical imaging etc. Considerable efforts are now directed for the progress of technology to provide thin films of such materials. It is now established that well poled polyvinylidene fluoride (PVDF) films show ferroelectric properties although their piezo and pyroelectric coefficients are significantly lower than those of ceramics, such as PZT, $BaTiO_3$, $LiNbO_3$ which suffer from poor mechanical strength. An intermediate approach is to design a polymer/ceramic composite in which a fine ceramic powder may be introduced in the matrix of a polymer. Such a composite may combine superior mechanical strength and electrical breakdown strength of a polymer with the excellent thermal, dielectric and electro-active properties of a ceramic.

Present work reports the results of a study of dielectric and pyroelectric properties and the nature of absorption and steady state currents of a flexible polymer-ceramic composite 'Piezel' which is manufactured by the Daikin Industries Limited of Japan and in which a ceramic has been introduced in the matrix of a polymer.

2. EXPERIMENTAL

Piezel samples were supplied with a nominal thickness of 155 microns. An x-ray diffraction study of the material indicates that the composite may consist of an inclusion of PZT in the matrix of a co-polymer of PVDF. The samples were cleaned with isopropyl alcohol and aluminium electrodes of area 1cm x 1cm were vacuum deposited on both surfaces of each sample, the electrode thickness being approximately 700 Å. These samples were then thermally treated in an evacuated measurement chamber ($<10^{-5}$ Torr) at 373K for 24 hours with their electrodes shorted. Such thermal treatment prior to an application of high electric fields (poling) tends to reduce significantly any residual or remanent internal polarization. Samples were then electrically stressed with external electric field in the range of $1.75 \times 10^{5} Vm^{-1}$ to $7.5 \times 10^{6} Vm^{-1}$ in the temperature range of 293K – 373K for 18 hours at each field at a pressure of $<10^{-5}$ torr. A Brandenburg type 472R high stability photomultiplier EHT supply was used for poling the samples. After poling the samples were discharged for three hours at the same temperature as that of the charging. The charging and discharging currents were monitored with a Cary electrometer, Model 401 and were also suitably recorded. Following the discharge, the samples were thermally conditioned again before the application of each of the specific poling fields.

The dielectric dispersion data were obtained using a General Radio Bridge (Type 1621 with a 1238 detector and a 1316 oscillator) in the frequency range of 10 Hz – 10^{5} Hz in the temperature range of 293K – 373K, the sample being maintained in the evacuated sample chamber.

The pyroelectric responses were studied with a direct method[1] and also by a dynamic method[2-5] for the composite films. In the direct method, a linear heating rate of the sample of approximately 1K/minute was maintained by adjusting the d.c. voltage supply to the heater. The dynamic pyroelectric response was obtained by exposing the smples to a step input of well focussed radiations from a tungsten filament lamp through a quartz window of the evacuated sample chamber. All pyroelectric measurements were made at the end of each discharging period with samples which have been previously charged at different fields and temperatures.

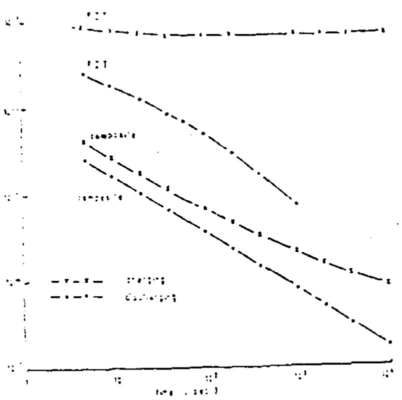
Absorption currents, pyroelectric studies and dielectric measurements were also made with PZT discs which were supplied by Unilator (U.K.).

3. RESULTS AND DISCUSSIONS

Figure 1 shows a typical set of charging $I_c(t)$ and discharging $I_d(t)$ current transients of the composite and the PZT at a high field of

Figure 1: Charging and discharging currents in PZT and composite.

$E = 7\times10^5$ Vm^{-1} $T = 343$ K



7×10^5 Vm^{-1} at 343K. The polarity of the discharging currents has been reversed for the purpose of a comparison with clarity. A detailed study of the current transients of the composite shows that the difference in magnitude of I_c (t) and I_d (t) at constant times increased with increasing charging fields and temperatures, probably due to an onset of quasi-steady state conduction current. The monotonic decay of the current transients also follow the well known expression:

$$I(t) = A(T)t^{-n} \qquad .....(1)$$

where A is a temperature dependent factor, t the time after application or removal of the external voltage and $n \lessgtr 1$.

The isochronal charging current (i.e. the current at constant times) obtained from such data as shown in figure 1, for the composite shows a non-linear behaviour at longer times and at high fields, thus indicating possibly a presence of ionic or electronic space charge.

It may be observed that the charging current in PZT reaches a steady state value at short times (~100s). The volume resistivity of PZT, calculated from these results, is observed to be approximately 3 x 10[illegible] ohm-metre which is about three orders of magnitude lower than that of the composite. From a study of the isochronal charging currents it may be suggested that the space charge is not the dominant mechanism for the origin of the steady state conduction in this material for the ranges of fields and temperatures employed in this work.

It has been shown[5] that the conduction process in PVDF at high temperatures and fields is best described by an ionic model. Assuming a model of diffusion of lattice defects or ions and a carrier hopping process Mott and Gurney[7] obtained the following expression for a steady state current I_s, for low fields:

$$I_s = I_o \exp(-\phi/kT) \sinh(edE/2kT) \quad \ldots\ldots \qquad (2)$$

where I_o is a constant, ϕ the activation energy, d the jump distance, E the electric field and the other symbols have their usual meanings. Equation (2) reduces to:

$$I_s = I_o \exp(-\phi/kT) \exp(edE/2kT) \quad \ldots\ldots \qquad (3)$$

which is similar to an expression derived by Lawson[8] for the high field dependence of I_s. Figure 2 shows typical plots of ionic conduction which were obtained from the present work with the composite and PZT. The value of the jump distance d was calculated in each case from the linear part of the curves. For PZT, the d-value was observed to be ≈700Å with the value of the activation energy of 0.65 eV which is in good agreement with that obtained by Heywang[9] in barium titanate. We assumed that the motion of a carrier from one crystallite to another occurs by a barrier hopping process. For the composite the d-value (≈450Å) and the activation energy (≈0.8eV) were observed to be similar to those of PZT, thus suggesting that the origin of steady state conduction is of ionic nature in both materials and that the role of PZT is dominant in the conduction process for the composite.

Fig.2 Ionic plot for PZT and composite at 343K

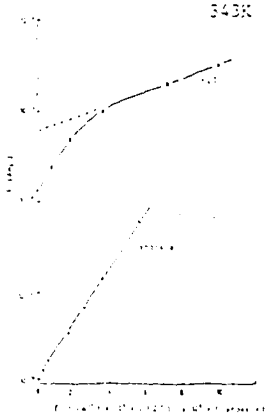
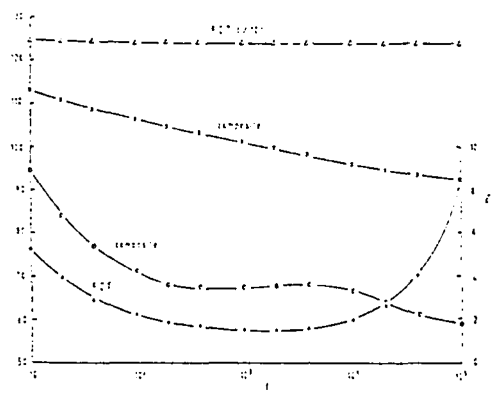


Figure 3 shows the behaviour of ε' and ε'' with frequency for PZT and the composite at 365K. In order to optimise the vertical scale the ε' - values of the PZT have been divided by 10. It may be observed that there is little change in the PZT permittivity (ε') over four decades of frequency. The high values of ε' of the ceramic is to be associated with the domain walls and the phase-boundary effects in which a build up of charges at the interface appears to be resulting in high capacitance of the material. The permittivity (ε') of the composite appears to decrease by 14% from its magnitude of 110 at

Figure 3. The behaviour of ε' and ε" against frequency PZT and composite at 363K.

ε'(Δ), ε"(o) = PZT ε'(X) ε"(·)= composite

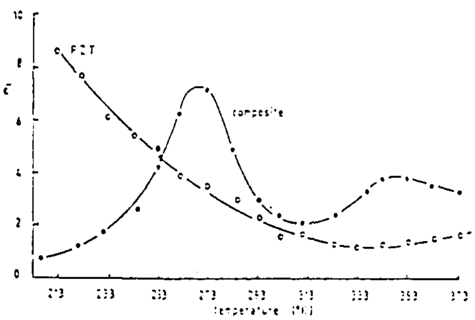


20Hz to 55 at 10^5 Hz. It should be noted that ε' of the composite is greater than that of PVDF by an order of magnitude over the same frequency range mentioned above. The ε" behaviour of PZT shows no relaxation (figure 3) in the four decades of the frequency range up to 100KHz which suggests that there is no appreciable phase boundary or domain wall effect. On the other hand, the ε" response of the composite shows a broad loss process which may be assigned to the relaxation of PVDF which occurs in the frequency range of $1-10^5$ Hz in the temperature range of 293-413K.

Thus the behaviour of the loss process in the composite may originate from the copolymer of PVDF rather than in the ceramic phase. The activation of this loss peak was observed to be approximately 1.2 eV which is in agreement with that of PVDF.

The temperature dependence of ε" of PZT and the composite at 1 KHz is shown in figure 4. It may be observed that there is a low temperature relaxation peak of the composite at 269K. This may be ascribed to the molecular motions in the amorphous phase of the polymer. It should, however, be noted that the observed temperature of this peak (269K) is considerably higher than that of PVDF at 233K[13]. This may possibly be due to the influence of PZT particles residing in the amorphous phase of the polymer. The second broad peak of the composite at ~353K is due to α_c-relaxation.

Figure 4: The behaviour of ε" against temperature in PZT and composite at 1kHz.



The ε"-behaviour of PZT shows no structure and a monotomic decrease with increasing temperature.

Now the time dependence of discharge current in a dielectric may be used to determine the dielectric loss factor using the following approximation due to Hamon[11].

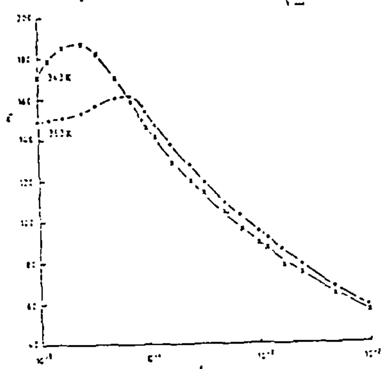
$$\varepsilon''(f) = \frac{I(t)}{2\pi f C_o V} \quad \frac{I(0.1/f)}{2\pi f C_o V} \qquad \ldots \qquad (4)$$

where $I(t)$ is the magnitude of the discharge current at a time t after the removal of voltage V, C_o the geometric capacitance of electrode geometry without the sample and f the Hamon frequency $(=0.1/t)$. This method has been employed in figure 5 to determine behaviour of the composite at low frequencies in the range 10^{-5} to 2×10^{-2} Hz. The observed location of the peak (figure 5) corresponds well to that of the polymer, thus suggesting again that the dielectric behaviour of the composite is in good agreement with that of the polymer.

In the direct method for the determination of the pyroelectric coefficient $p(T)$ a poled sample is heated at a constant rate of

Figure 5: Low frequency characteristics of ε" in composite.

pre- E: 5.6×10^{5} Vm^{-1}



temperature rise with its electrodes shorted and the pyroelectric current Ip, is given by:

$$Ip = ap(T)\frac{dT}{dt} \qquad \ldots \qquad (5)$$

where a is the sample area and dT/dt is the time rate of change of temperature. The value of the pyroelectric coefficient was determined in the present work after three thermal cycling of temperature to establish a measure of the reversible pyroelectricity. The value of p(T) at 323K for the composite was observed to be 3.5×10^{-5} C/m^2 °C which is significantly higher than that of PVDF ($\sim 8 \times 10^{-6}$ C/m^2 °C) at the same temperature.

In the dynamic method[2] the pyroelectric coefficient is given by the following expression,

$$Ip\ (max) = Kp(T) \qquad \ldots \qquad (6)$$

where

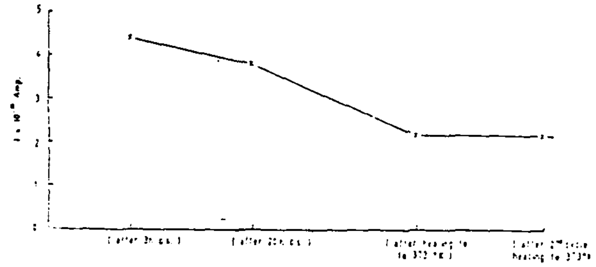
$$K = \frac{F_o a}{\rho Cpd}\,\theta\left(\frac{\theta}{1-\theta}\right)$$

where Fo is the radiation power absorbed per unit area of the electorded sample, a the electrode area, ρ the density of sample, Cp the specific heat, d the sample thickness, Ip(max) the peak value of the pyroelectric current and $\xi = \tau_e/\tau_T$ where τ_e and τ_T are the electrical and thermal time constants of this system respectively. Ip (max) has generally been measured in the present work in the following manner.

The sample is charged at 323K for 28 hours at a suitable potential. It is then discharged for 20 hours at the same temperature. Ip (max) is then measured by illuminating the sample surface with a step input of thermal radiation. In order to observe the behaviour of the irreversible and reversible pyroelectricity Ip(max) was measured (i) after 3 hours of discharge, (ii) after 20 hours of discharge, (iii) following 20 hours of discharge at 323K and subsequent heating of the sample at 373K and (iv) finally after two thermal cycling of the sample from 300 - 373K after 20 hours of discharge. The results are shown in figure 6 from which it may be

Figure 6: Behaviour of pyroelectric peak current in composite at various times and after thermal treatment.

Sample was charged for 28h at 2kV, 323°K and discharged at 323°K. Points were measured at 323°K.



observed that a decay of 12% of Ip(max) was observed after 20 hours of discharge compared to that after 3 hours of discharge. A further reduction of Ip(max) of about 50% occurs after the sample is heated to 373K with its electrodes shorted. No further decay of Ip(max) was observed on subsequent thermal cycling, thus establishing a stable and reversible pyroelectricity in the composite. Further work is necessary to determine p(T) by the dynamic method as the magnitude of Cp is not accurately known for the composite.

In conclusion, it is suggested that the steady state conduction behaviour in the polymer - ceramic composite may originate from an ionic hopping mechanism which is dominated in the PZT phase. However, the dielectric loss process may be largely due to the polymer phase with some significant contribution by the PZT phase at low frequencies and high temperatures. The pryro-electric coefficient of the composite has been observed to be significantly higher than that of PVDF.

Acknowledgement

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Electrical and dielectric properties of polymer–ceramic composites

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ABSTRACT: Composites of Lead Zirconate Titanate (PZT) and polyvinylidene fluoride (PVDF) were prepared and its electrical and dielectric behaviours were analysed. PZT phase has been suggested to have a significant contribution on the electrical conduction and low frequency dielectric loss at high temperatures. The pyroelectric behaviour obtained from composites of different materials may suggest that the elastic stiffness and thermal expansion of the polymer matrix were among the factors contributing to the measured pyroelectric activity. A higher pyroelectric figure of merit as compared to PZT has been achieved in one of the PZT/PVDF composites.

1. INTRODUCTION

Ferroelctric composites of ceramic and polymer have lately received considerable attention due to their advantages in piezoelectric properties for transducer applications (Skinner et al 1978, Newnham et al 1980). There are many ways in producing ceramic/polymer composites (Newnham et al 1978) but the simplest method is by introducing the ceramic particles into the polymer matrix. In this type of composite, the ceramic particles are not in contact with each other while the polymer phase is self-connected thus having formed a 0-3 connectivity (Newnham et al 1978). The ceramic/polymer composites thus constitute a new structure which might differ in many respects from their single phase components. Hence the design of the composites with optimum properties becomes very challenging since its properties do not only depend on the materials and the compositions but also on their interconnections. Present work reports the results of a study of the electrical and dielectric properties in PZT/PVDF composites.

2. EXPERIMENTAL

Composite samples are prepared from PZT ceramic powder (PZT5 and PZT8, supplied by Unilator, U.K.) mixed up with PVDF pellets (PVDF(A) is solef 11010 and PVDF(B) is solef 1008, obtained from Laporte Trad., U.K.) at 443K using a hot roller machine and then pressing into film of 250 μm in a temperature-controlled hydraulic press. After depositing an aluminium electrode of 2cm x 2 cm on both sides of the film, the samples were thermally treated in an evacuated measurement chamber ($<10^{-5}$ torr) at 373K for ~24 hours before any measurements were performed. The dielectric permittivity and the dielectric loss were measured using a General Radio Bridge or a Solartron FRA. Pyroelectric activity was measured by a direct method (Byer and Roundy 1972), in which a linear heating rate of $1^{\circ}C$/min is employed. The pyroelectric responses were also studied by a dynamic method (Simhony and Shaulov 1971, Das-Gupta and Doughty 1980) by exposing the samples to a well focused light from a tungsten filament. Some results obtained on PIEZEL (composite of PZT and PVDF copolymer, supplied by Daikin Industries Limited of Japan) are also presented.

3. RESULTS AND DISCUSSIONS

The time dependence of charging currents in PZT/polymer composites are shown in Figure 1. It may be observed that in all cases the currents decreasing monotonously with the time at different rates

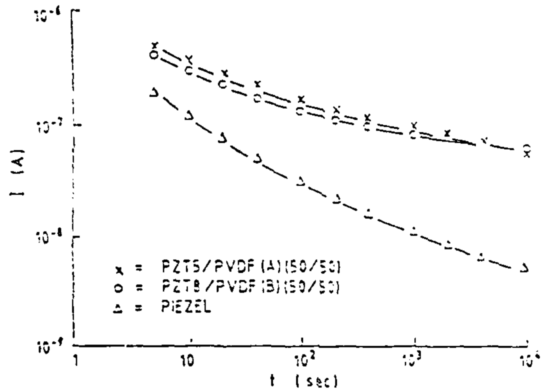

Fig. 1: Charging currents in PZT/PVDF and PIEZEL at 363K and field 1.75×10^6 Vm^{-1}.

of decay. However, for the two upper curves which were obtained using different types of PZT and different PVDF grades of equal volume percentage between ceramic and polymer phases, the difference is not so significant. The current in PIEZEL sample was observed to reach steady state level in the region of ~10^5 sec whereas in the prepared composites the time taken is shorter. Indeed, the steady state level could be reached at earlier times as the temperature and field are increased. The analysis of the steady state current in the composites showed that its behaviour is governed by an ionic hopping mechanism with a substantial contribution from PZT phase at high temperatures (Das-Gupta and Abdullah 1986, Das-Gupta and Abdullah 1987).

Figure 2 shows the behaviour of the dielectric permittivity and loss in the composites. In the high frequency region, the values of ε' are about the same for all composites but at the lower

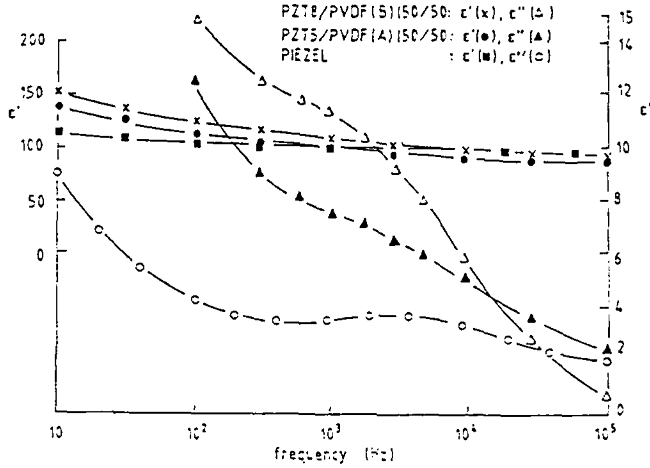

Fig. 2: The behaviour of ε' and ε" against frequency in PZT/PVDF and PIEZEL at 363 K.

frequencies, their values tend to differ significantly. The calculated permittivities of the prepared composites using the equation given by Yamada et al (1982) are in good agreement with the observed values (Das-Gupta and Abdullah 1987). The dielectric loss behaviour shows a broad peak in the region 10^3-10^4 Hz which may be due to the relaxation of the polymer phase which occurs at similar frequencies and temperature region. The high dielectric loss at lower frequencies seemed to be significantly due to PZT phase as had been revealed in the previous results (Abdullah and Das-Gupta 1987, Das-Gupta and Abdullah 1987).

The large difference of losses at lower frequencies between those composites may be due to the different types of PZT being employed which may arise from their differences in microstructures (domain walls, crystallite size and grain boundaries). Furthermore, the added impurities (which are usually present and of diffent kinds for diffent PZT types) into the PZT phase may also cause such a big difference of ε" values (Lines and Glass 1979).

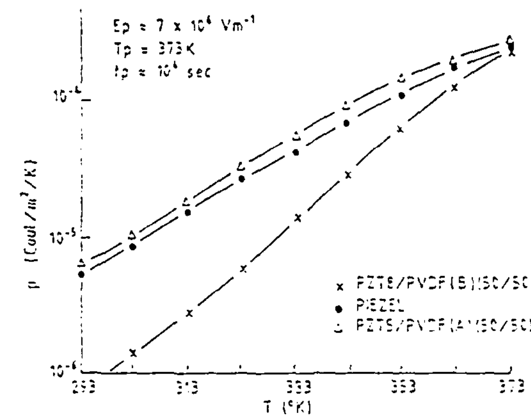

Fig. 3: Pyroelectric coefficient against temperature in PZT/PVDF and PIEZEL.

The pyroelectric coefficients as a function of temperatures obtained by the direct method in the composites are shown in Figure 3 from which it may be observed that the sample with highest losses

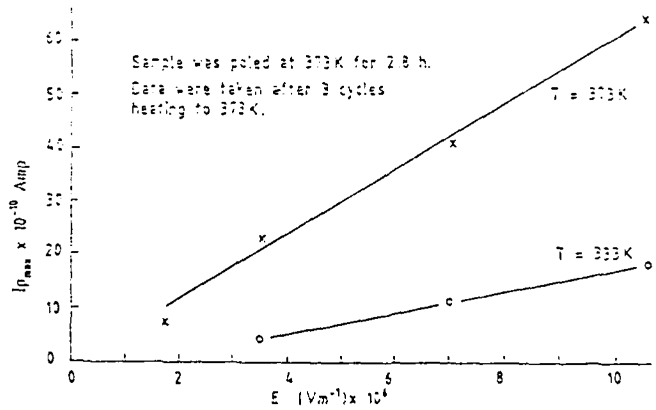

Fig. 4: Peak current against poling field in PZT5/PVDF(A)(50/50).

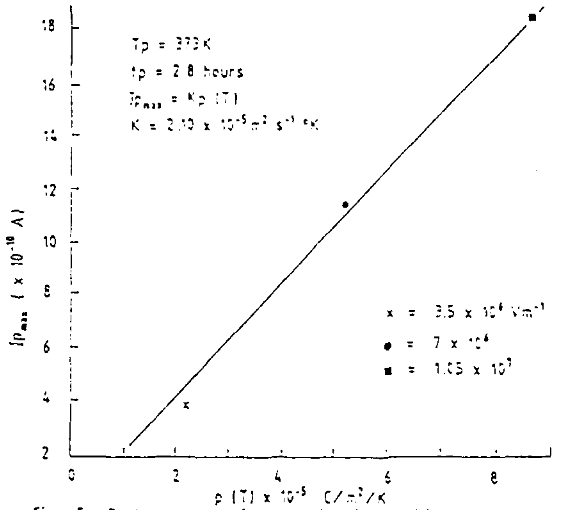

Fig. 5: Peak current against pyroelectric coefficient at 333K in PZT5/PVDF (A) (50/50).

showed a very low p(T) at lower temperatures region, whereas the other two samples appear to have similar p(T) values. Factors such as elastic stiffness and thermal expansion of the polymer and the interconnection and internal stresses may contribute significantly to the observed differences in p(T) values of the present results, in the same manner as the result of Galgoci et al (1986) showed. For composite PZT5/PVDF(A), although the value of p(T) at 343K is only 9×10^{-5} Coul/m^2/K which is lower than that of PZT (p(T) = 50×10^{-5} Coul/m^2/K) at the same temperature, its pyroelectric figure of merit $p(T)/\varepsilon'$ is 2.5 times higher than that of PZT (taking ε'(Composite)=95, ε'(PZT)=1300). Figure 4 shows the pyroelectric peak current Ip_{max} obtained by the dynamic method as a function of poling fields at 373 K and 333 K in PZT5/PVDF(A). It may be observed that the data shows an approximately linear relationship at the temperatures and within the range of fields of the measurements. Obviously efficient poling is achieved at high temperatures and fields as long as it does not reach the breakdown field of the samples. Further measurements on PZT5/PVDF(A) established a linear relationship between Ip_{max} and p(T) at 333K (see Figure 5) as:

$$Ip_{max} = Kp(T) \qquad (1)$$

where $K = 2.1 \times 10^{-5}\ m^2.s^{-1}.^{o}K$, which could be considered as a constant for the same sample material having the same electrode geometry with the incident light power and the electrical and thermal time constant of the system remain unchanged.

In conclusion, the steady state conduction of PZT/PVDF composites and its dielectric loss in the low frequencies region at high temperatures are significantly controlled by PZT phase. A higher pyroelectric figure of merit has been achieved in one of the composites of PZT/PVDF as compared to single phase PZT.

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PREPARATION AND CHARACTERIZATION

POLYMER-CERAMIC COMPOSITE MATERIALS WITH HIGH DIELECTRIC CONSTANTS

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The possibility of employing thick film composite materials for capacitor dielectrics has been investigated using a system in which high permittivity ceramic powders (lead zirconate titanate) have been incorporated in a polymer matrix (poly (vinylidene fluoride)). The results indicate that it is possible to produce flexible composite materials with dielectric constants two orders of magnitude greater than those of capacitor grade polymers such as polypropylene. Commercial exploitation of such materials will depend on the choice of ceramic material, its availability with a small particle size (less than 10 μm) and good control of processing in order to produce a good surface texture and a low concentration of voids which might enable high fields to be applied without breakdown.

1. INTRODUCTION

The constant movement towards the miniaturization of electronic circuitry coupled with the need to store larger energies in capacitor systems has fuelled a search for new dielectric materials which will enable a high energy density to be realized. The present generation of low leakage capacitors employs thin films of non-polar polymers such as polypropylene which have a very low relative permittivity of about 2 but can withstand very high fields[1]. Indeed, the breakdown field increases with decreasing thickness down to a few microns although the resistance of such films to heat damage is not great.

High permittivity ceramics have been traditionally used in high voltage capacitors because of their high breakdown voltages. However, they suffer from poor mechanical strength and therefore cannot be exposed to high fields. This effectively means that they cannot be miniaturized.

Considerable research effort is today directed towards specially grown thin films of materials such as aluminium oxide which might provide both a high dielectric strength and a high permittivity[2]. However, such materials are not yet available commercially and their properties are as yet not fully established. Furthermore, the technology is not available for producing such materials in the areas and thicknesses required for commercial applications in capacitors.

Hence, the intermediate approach has been to employ a composite material which might combine the superior mechanical, breakdown and fabrication properties of a polymer with the excellent thermal and dielectric properties of a ceramic. A composite material would thus be formed by introducing a ceramic and fine-powder form into the matrix of a suitable polymer.

In the present work the results obtained for a system in which small particles of lead zirconate titanate (PZT) have been mixed with poly(vinylidene fluoride) (PVDF) are reported. These materials may not be the most suitable combination for a capacitor grade composite but represent good examples of their material classes. They are also known to be mutually compatible and might have other applications in the field of composite piezoelectricity.

2. EXPERIMENTAL DETAILS

PZT powder with an average grain particle size of 20 μm was purchased from Unilator Technical Ceramics of Ruabon, U.K. Pellets of PVDF were kindly supplied by Laporte Industries of Luton, U.K. They were mixed in various concentrations using a rolling mill operated at 433 K. The composite hides were then pressed in a temperature-controlled hydraulic press to thicknesses in the range 100–800 μm. The use of high quality chromium plates for pressing allowed the production of films with a good surface texture. Samples were thoroughly cleaned with ethyl alcohol in an ultrasonic bath to remove all surface contaminants. They were then annealed in an oven for 72 h at 353 K to condition them. These processes were found to improve repeatability and increased both bulk and surface breakdown strengths.

In order to perform dielectric and conduction measurements, samples were furnished with circular aluminium electrodes of 0.1 μm thickness and 24 mm diameter by vacuum evaporation. Some tests were also performed with gold electrodes but no variation was found. We were also kindly supplied with discs of PZT by Unilator which were already furnished with fired silver electrodes of 2 μm thickness.

Experimental measurements were all performed in a stainless steel vacuum chamber at a pressure of less than 10^{-5} Torr. Temperature control to within 0.25 K was established using a Eurotherm controller. A high voltage was applied to samples from a Brandenburg photomultiplier supply and the currents were measured with a Keithley (model 616) digital electrometer suitably interfaced to a microcomputer (Acorn BBC) which stored data, plotted curves and performed transformations on line.

Dielectric measurements were performed either manually in the frequency range 10 Hz–100 kHz using a General Radio Bridge system (model 1621) or remotely using a microcompressor-controlled system evolved from a Solatron model 1250 frequency response analyser. This latter system was capable of scanning the frequency range from 0.01 mHz to 65 kHz with a high resolution.

The samples produced by milling and pressing tended to be brittle when the PZT proportion was high (greater than 60 wt %). This could lead to great difficulties when thin films are required, especially if the dielectric is required to conform to some curved or otherwise complicated surface. A possible solution to this problem is the incorporation of a third material in the composite in order to provide increased flexibility. A fluoro-elastomer may have the necessary properties for this application but a plasticizer may be easier to incorporate into a matrix of the type employed here.

We have investigated the use of plasticized samples in a limited manner. We first partially dissolved PVDF pellets in a warm mixture of methyl sulphoxide and dimethyl formide solvents to which measured quantities of trioctyl phosphate and dioctyl phthalate plasticizers were added. On cooling, a suspension of PVDF was obtained which could be mixed easily with PZT powder to form a composite. The mixtures were allowed to dry slowly in a flow of moist nitrogen and then were pressed into thick films (100 μm thickness) at room temperature. These were then vacuum dried for 24 h to remove all traces of solvent before being conditioned at 333 K to improve texture. The films were electroded and their characteristics measured in the manner described above.

3. RESULTS AND DISCUSSION

Typical charging and discharging transients for PZT and a composite sample with a high (75%) PZT content are shown in Fig. 1. It may be observed that at 333 K and for a low field of 0.16 $MV\,m^{-1}$ a steady state conduction current is achieved within 1000 s. Similar behaviour was found at all temperatures above 313 K and for the range of fields investigated in the present work. The charging currents for the composite material may be observed to decrease monotonically with time for at least 10 000 s.

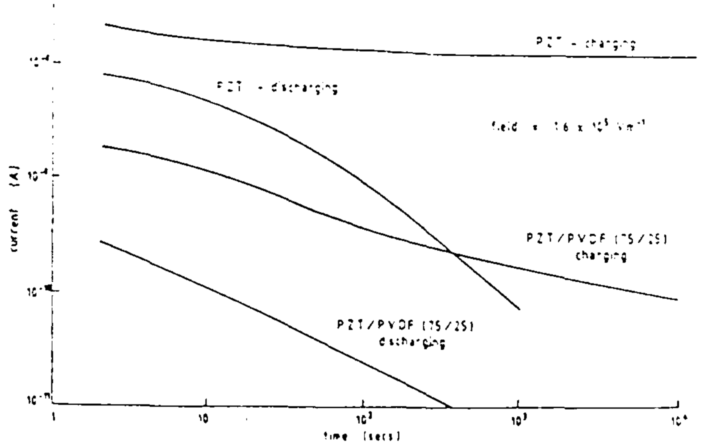

Fig. 1. Charging and discharging current transients in PZT and in a 75 vol% PZT composite at 333 K (field, $1.6 \times 10^5\ V\,m^{-1}$)

Figure 2 shows similar data for pure PVDF and for a composite sample containing equal values of PVDF and PZT. The charging currents are lowest for PVDF and it may be observed that the current after 10 000 s increases as the proportion of PZT is increased.

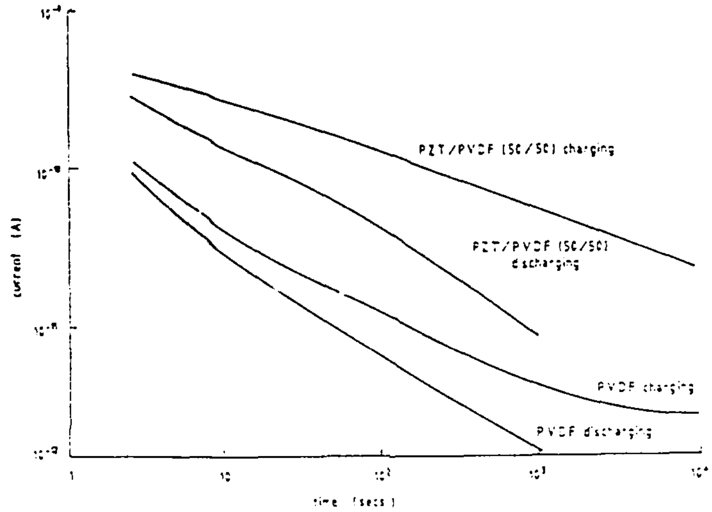

Fig. 2. Charging and discharging current transients in PVDF and in a 50 vol.% PVDF composite at 333 K (field, 1.6×10^{7} V m^{-1}).

The discharge currents observed when the applied field was removed were opposite in polarity to the charging currents in all cases and were smaller in magnitude. This suggests that the dominant mechanism responsible for such currents was dipolar reorientation. In all cases except for pure PZT, the transient current dominated the conduction current.

The discharging current transients may be transformed into the relevant low frequency dielectric loss information using Fourier analysis or by the Hamon[3] approximation. The loss factor ε'' at frequency f is related to the discharge current I_d at time t s following the removal of the field $E (= V/d)$, where V is the voltage and d the thickness, by the equation

$$\varepsilon''(f) = \frac{I_d(t)}{2\pi f C_0 V} = \frac{I_d(0.1/f)}{2\pi C_0 V} \tag{1}$$

where C_0 is the geometric capacitance of the electrode assembly without the sample, V the magnitude of the step voltage and f the Hamon frequency given by

$$f = \frac{0.1}{t} \tag{2}$$

The approximation is only valid provided that the charging time exceeds the recorded discharging time by about an order of magnitude. In the present work the charging time was 10000 s which allows us to transform discharging data up to 1000 s and provides low frequency loss information to frequencies as low as 10^{-4} Hz.

Low frequency loss spectra for PZT, PVDF and a 50 vol.% PZT–50 vol.% PVDF composite sample are shown in Fig. 3 in which the loss factors for PVDF and for the composite sample have been multiplied by a factor of 10 in order to improve clarity. A peak may be observed for PZT in the vicinity of 1 mHz and with a magnitude of 90. This may be due to ionic impurities, to the motion of protons or to the presence of electronic space charge which may be trapped at domain walls. This last possibility may be quite likely in a ferroelectric material such as PZT which is highly polar. No peak may be observed in the other materials but it is probable that the loss process does peak at this temperature but at a lower frequency and outside the range investigated in the present work. This is consistent with our earlier work in which we observed the α_c relaxation in PVDF at 0.1 mHz at 353 K. This has been attributed to an interfacial polarization at crystalline–amorphous boundaries or to the rubbery flow of polymer chains. The similarity between the low frequency behaviour of the composite material and that of pure PVDF suggests that the polymer properties dominate the dielectric behaviour of the polymer.

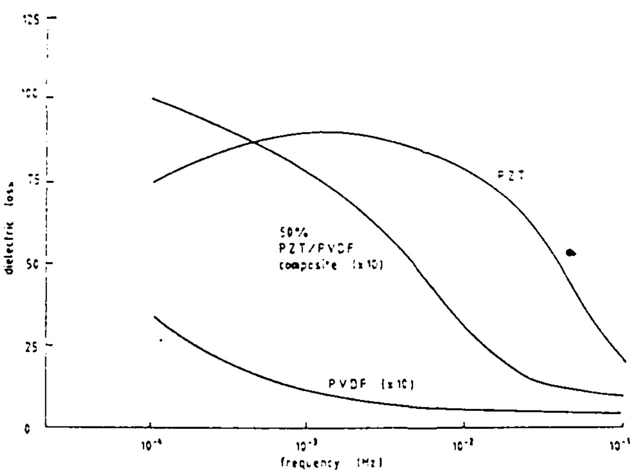

Fig. 3. Low frequency dielectric loss spectra for PZT, PVDF and the composite at 333 K using the Hamon approximation

We have shown elsewhere[4] that the conduction process in PVDF at high temperatures and at high fields is best described by an ionic model with an average jump distance of 2.5 nm. The electrical conduction in a crystalline ceramic such as

PZT is also ionic and it appears likely that the conduction in a composite of these materials would also be ionic. We have investigated this behaviour by analysing the field dependence of the conduction current both in PZT and in a composite, and the ionic conduction plots are presented in Fig. 4 and 5 respectively.

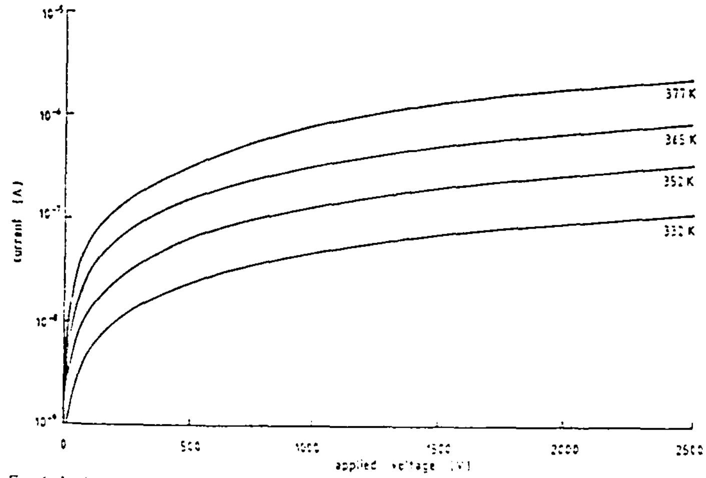

Fig. 4. Ionic conduction plot for PZT.

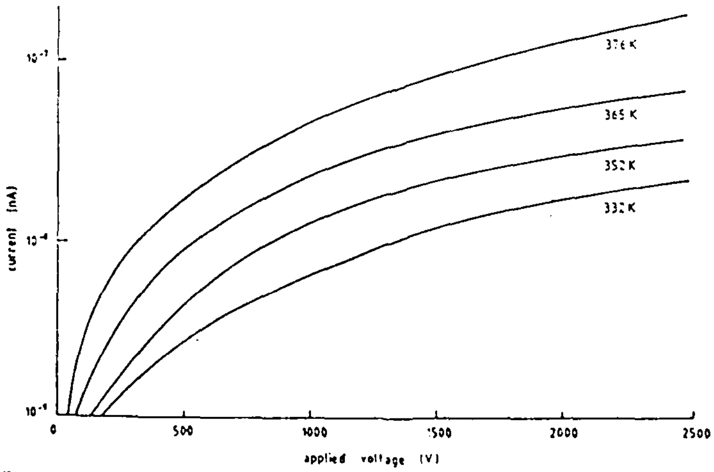

Fig. 5. Ionic conduction plot for a PZT-PVDF composite.

According to Lawson[5], the high field dependence of the ionic conduction current I_i is given by an expression of the form

$$I_i(T) = I_0(T)\exp\left(\frac{ejE}{2kT}\right) \tag{3}$$

where I_0 is a temperature-dependent constant incorporating the thermal activation energy, e is the electronic charge, j is the jump distance and k is Boltzmann's constant. Hence, plots of log I_i *vs.* E or voltage should yield straight lines from which the average jump distance may be evaluated. From the gradients over the linear portions of Figs. 4 and 5 the average jump distances in PZT and in the composite were calculated to be 46 nm and 43 nm respectively with an uncertainty of 5 nm. These results seem to indicate that the role of PZT is dominant in the conductivity of the composite. However, the analysis given above should be treated with some caution as the range of fields employed may not extend to a sufficiently high level to ensure that an ionic mechanism operates. Indeed, the deviation from ohmic behaviour was observed to be only slight in the case of PZT. In the present work we have deliberately not considered alternative models such as the Schottky effect and Poole–Frenkel conduction as these may not be appropriate in polymer systems below fields of the order of 10 MV m^{-1}. It may, of course, be necessary to consider such processes with the thinner films which may be appropriate to capacitor systems.

The dielectric constant for a two-phase system with spherical dispersions has been expressed by the formula[6]

$$\varepsilon = \frac{2(1-x)\varepsilon_1 + (1+2x)\varepsilon_2}{(2+x)\varepsilon_1 + (1-x)\varepsilon_2}\varepsilon_1 \tag{4}$$

where x is the volume fraction of the inclusion, and ε_1 and ε_2 are the dielectric constants of the respective phases. We refer to this as formula A for the determination of the dielectric constant. This is a general formula for mixtures. In our examples, the dielectric constant of the filler (phase 2) is much larger than the dielectric constant of the continuous phase. Hence, we may simplify eqn. (4) by omitting all reference to the dielectric constant of the ceramic. This leads to the reduced equation[7]

$$\varepsilon = \frac{1+2x}{1-x}\varepsilon_1 \tag{5}$$

We refer to this as formula B.

In Fig. 6 we have plotted the experimental values of the relative permittivity of the composites as a function of the volume fraction of PZT. These data were obtained at a frequency of 1 kHz. In general, the values would be expected to be higher at lower frequencies. On the same graph, we have drawn the theoretical permittivity curves using the above formulae. It may be observed that a linear model would be superior to either model A or model B but that model B provides a closer fit than model A does at high volume fractions of PZT. This result suggests that the permittivity of the ceramic is, indeed, unimportant and that we need to consider only the polymer when fabricating a high permittivity composite.

The above analyses are based on the assumption that the ceramic powders may

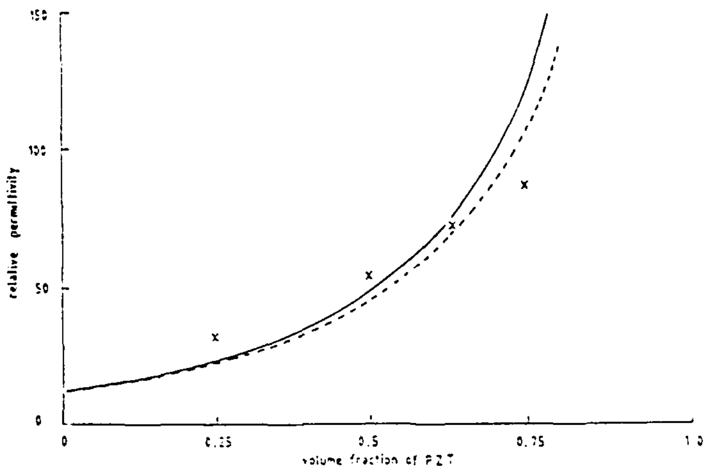

Fig. 6. Theoretical (——, model A; - - -, model B) and experimental (×) dependences of permittivity on the volume fraction of PZT.

be regarded as a spherical inclusion in an amorphous polymeric matrix. This will not generally be the case because of the spherulitic properties of a semicrystalline polymer which may influence the binding sites and because the structure of the ceramic particles may not be consistent with spherical symmetry. Processing by drawing or rolling may also have an effect. This possibility may be accounted for in a binary system by assuming that the included particles are ellipsoidal, the principal axis being in the x direction[8].

This produces a more complex expression for the permittivity of the composite:

$$\varepsilon = \frac{Nx(\varepsilon_2 - \varepsilon_1)}{N + (\varepsilon_2 - \varepsilon_1)(1 - x)} + \varepsilon_1 \tag{6}$$

Most of the symbols are as previously defined above and N is a shape parameter which can be adjusted to fit the experimental data.

In Fig. 7 we have replotted the experimental permittivity data for the composite sample as a function of the volume fraction of PZT. We have also drawn theoretical curves corresponding to eqn. (6) for various values of the shape parameter N. It may be observed that no curve passes through all the experimental data points but that the $N = 3$ case provides the best fit. This is effectively the spherical case which implies that this more complex model may be no better than model B. It is possible that the shape parameter may itself be a function of the volume fraction of ceramic. Physically, this could be a consequence of particle attraction or of differing distortion as a result of hot pressing. It is interesting to note that eqn. (6) reduces to a linear model when $N = 0$. However, this is not a reasonable possibility in the present case and it would require the polymer to have zero permittivity.

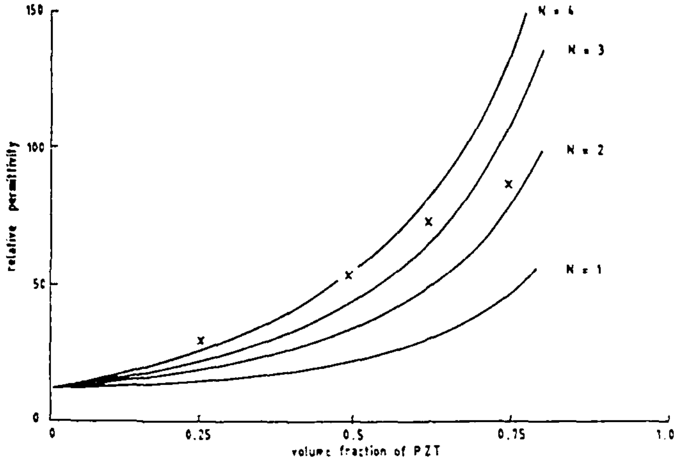

Fig. 7. Effect of particle shape on the permittivity of composite material: ×, data.

As mentioned previously, the experimental values cited above are those measured at 1 kHz. For capacitor applications, lower frequency information may be more relevant, especially if device operation is to be at mains frequencies (50–60 Hz). In Fig. 8 we present the frequency dependence of the relative permittivities of PZT,

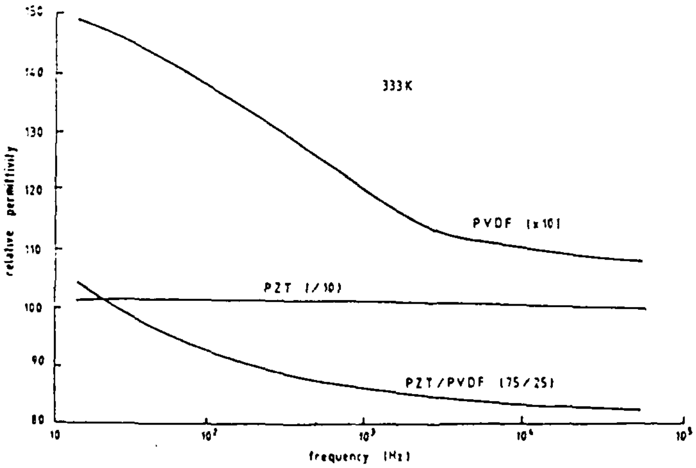

Fig. 8. Frequency dependence of permittivity in PZT, PVDF and a composite material at 333 K.

PVDF and a composite of the two materials. In order to optimize the vertical scale we have multiplied the PVDF data by 10 and divided the PZT data by 10. It may be observed that there is little percentage change in the PZT permittivity over four decades of frequency. In contrast, the permittivity of pure PVDF increases by nearly 40% as the frequency is decreased from 100 kHz to 10 Hz. The behaviour of the composite material is similar to that of the polymer alone and it may be observed that values of permittivity in excess of 100 may be obtained at the lower frequencies.

In order to explain the frequency dependence of the dielectric properties, we have plotted the frequency dependence of the dielectric losses of PZT and of PVDF in Fig. 9 at 333 K. The α_c process in PVDF[9] may be observed to peak at about 80 Hz, whilst a broad process is evident in PZT. Although the relative magnitudes of the loss processes are similar, the process in the polymer is more significant because it implies a loss tangent of 0.1 compared with 0.001 in PZT.

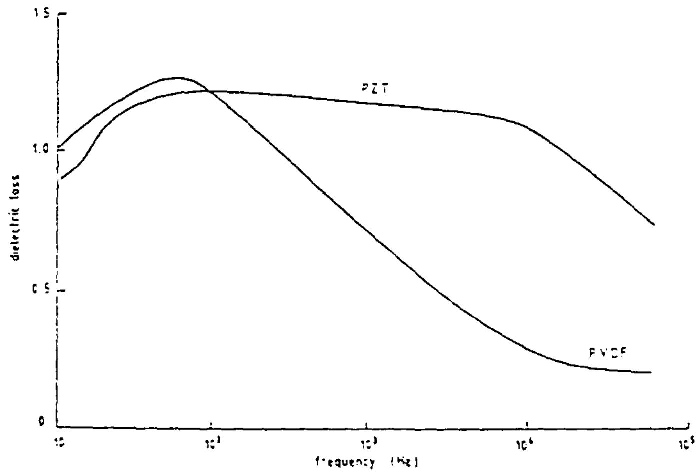

Fig. 9. Frequency dependence of the dielectric loss in PZT and PVDF at 333 K.

The frequency dependence of the loss process in the composites is shown in Fig. 10. The behaviour is again similar to that of the polymer up to 50% PZT content. No peak may be observed in the 75% PZT case but this may be simply because of the increasing ionic effect or the presence of an interfacial polarization. However, it may be significant that the actual level of dielectric loss increases as the fraction of PVDF decreases. We believe that this may be the result of decreased steric hindrance in the presence of a filler rather than some more specific interaction mechanism.

Finally, we have performed some preliminary measurements on plasticized composites. These samples showed superior mechanical properties and were easier to process than the simple binary sample. However, it was possible that the effect of

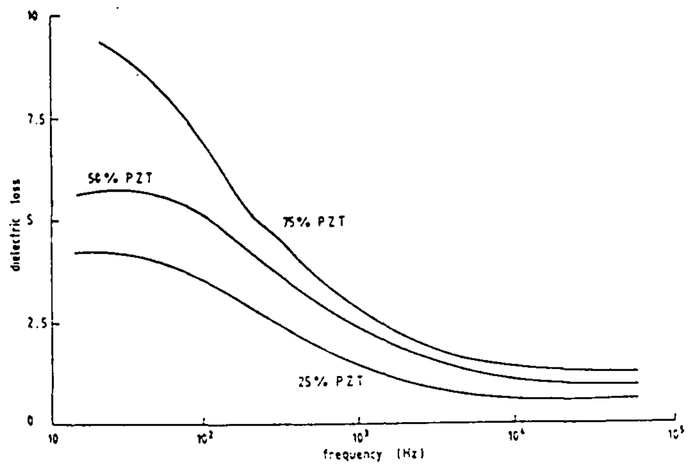

Fig. 10. Frequency dependence of the dielectric loss in various composite materials at 333 K.

the plasticizer would be to increase the conductivity to such an extent that the end product would be too lossy for practical applications. As plasticizers also effect the glass transition temperature, it was also possible that additional dielectric loss processes would be introduced or that existing processes would be shifted to less

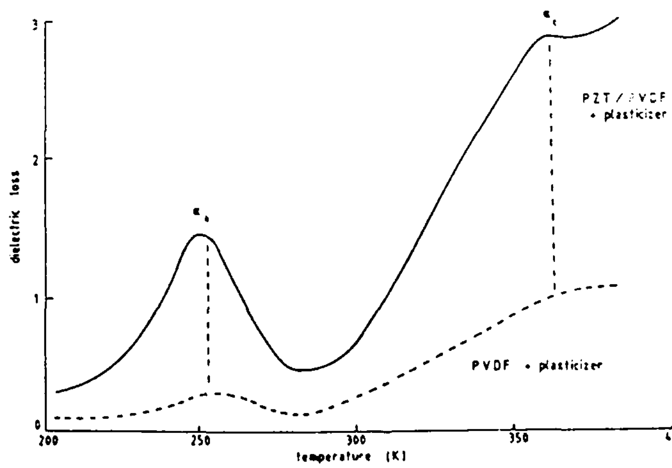

Fig 11. Temperature dependence of the dielectric loss in plasticized PVDF with and without PZT (frequency, 1 kHz).

favourable temperatures or that their magnitudes would become exceedingly large. The results shown in Fig. 11 prove that this is not the case. From the temperature dependence of the dielectric loss, only two peaks may be observed both for the PVDF–PZT–plasticizer and for PVDF with plasticizer only. These peaks agree well in terms of temperature and frequency with the two fundamental relaxations of PVDF, the α_a and the α_c processes. These are believed to be due to molecular motions in the amorphous and crystalline regions respectively.

It may be observed from Fig. 11 that both the above processes are considerably increased in intensity by the addition of PZT but that the effect of the plasticizer is comparatively insignificant. Hence, there may be no deleterious effect of adding an agent to increase flexibility. It may also be of interest to note that the α_a process is affected more by the presence of the PZT than the α_c process is. The reason for this is not clear but would most probably be because the PZT particles find their way preferentially into the amorphous phase. The α_c process appears to be associated with chain folds and, hence, might be more influenced by mechanical orientation[10] or by the dipolar alignment in a high d.c. field[11].

4. CONCLUSIONS

We have prepared composite materials by combining a high permittivity ceramic with a thermoplastic. The resulting samples can be processed adequately with simple apparatus but tend to become brittle when the ceramic content is high. The addition of plasticizer or elastomer improves the mechanical characteristics without decreasing the electrical strength. Relative permittivities of the order of 100 can be obtained with these materials provided that the dielectric constant of the polymer is sufficiently high. Although the electrical conductivity of the composite is governed by the ceramic, the dielectric properties are similar to those of the polymer.

For capacitor-type applications it is necessary to employ small particles of a high resistivity ceramic incorporated into a matrix containing a mixture of a high permittivity polymer with a rubber, plasticizer or elastomer. Care must be taken to ensure that no dielectric relaxation occurs around room temperature at the frequency of interest.

ACKNOWLEDGMENT

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APPENDIX A: NOMENCLATURE

C_g geometric capacitance
d sample thickness
e electronic charge
E electric field
f frequency
I_d discharging current
I_c conduction current
I_0 temperature-dependent constant
j jump distance
k Boltzmann's constant
N shape parameter of filler particles
t time
T temperature (K)
V voltage
x volume fraction of filler
ε permittivity of composite
ε_1 permittivity of the polymer (matrix phase)
ε_2 permittivity of the PZT (filler phase)
ε'' dielectric loss factor

Dielectric and pyroelectric properties of polymer/ceramic composites

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Ferroelectric ceramics such as Lead Zirconate Titanate (PZT) and $BaTiO_3$ have high dielectric permittivity, high piezo and pyroelectric coefficients and high electromechanical coupling which make them very useful in numerous applications, notably in high energy storage capacitors, acoustic emission detection, vidigon targets, medical imaging systems etc. However, their poor mechanical strength and relatively high value of acoustic impedance have restricted their use in some applications. On the other hand, piezoelectric polymers such Polyvinylidene Fluoride (PVDF) and its copolymer with trifluorethylene (TrFE) have relatively low acoustic impedance which could provide a good acoustic matching to water or tissues. Moreover, its good mechanical strength makes it a very attractive material, although its piezo and pyroelectric coefficient are relatively low as compared to ceramics. Therefore, a ferroelectric composite may be designed to combine the superior electro-active properties of the ceramics and the mechanical properties of polymers.

The composites can be prepared by several methods, such as by embedding a piezoelectric rod ceramic in a polymer matrix, by a replamineform process and by mixing ceramic and polymer phases together at certain temperatures [1–3]. The latter method is convenient as the composite could be prepared to any desired size and composition. The present work reports the result of a study of absorption currents as well as the dielectric and pyroelectric properties of PZT PVDF composites.

Composite samples were prepared from PZT ceramic powder (obtained from Unilator, UK) mixed up with PVDF (grade Solef 11010, supplied by Laporte Trad., UK) at 443 K using a hot roller machine. The film was then pressed to approximately 200 μm and an aluminium electrode of 2 cm × 2 cm was vacuum evaporated on both sides of the film. The samples were then thermally treated in an evacuated measurement chamber (< 10^{-6} torr) at 373 K for 24 hours, before current absorption measurements were performed. The dielectric dispersion measurements were made using a General Radio Bridge (type 1621) or using a system comprising of a Solartron frequency response analyser and BBC microcomputers which have recently been developed at UNCW, Bangor. The pyroelectric currents were measured using a direct method [4] by applying a linear heating rate of approximately 1 °C min^{-1} to the samples which have been poled appropriately. Absorption currents and dielectric measurements were also made with PZT discs and

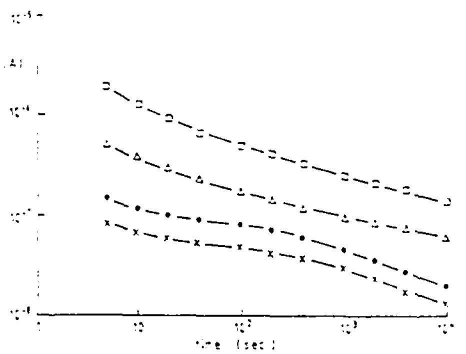

Figure 1 Charging currents in PZT PVDF (50:50) at different fields at 363 K. (×) 1.75 × 10^6 Vm^{-1}, (●) 3.5 × 10^6 Vm^{-1}, (△) 1.75 × 10^6 Vm^{-1}, (□) 7 × 10^6 Vm^{-1}.

piezel (a composite of PZT and PVDF copolymer, marketed by Daikin Industries Ltd, Japan).

Fig. 1 shows a set of charging currents at different fields at 363 K in a PZT PVDF composite with 50 vol % PZT. It may be observed that the current decreases progressively in time; however, at longer time and higher fields the rate of decrease is reduced possibly due to the tendency to reach a steady state level. The observed broad peak at low charging fields,

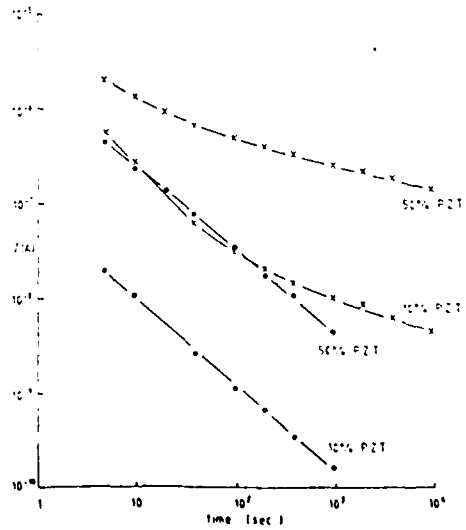

Figure 2 Charging (×) and discharging (●) currents in PZT PVDF at different compositions at 363 K with poling field 7 × 10^6 Vm^{-1}.

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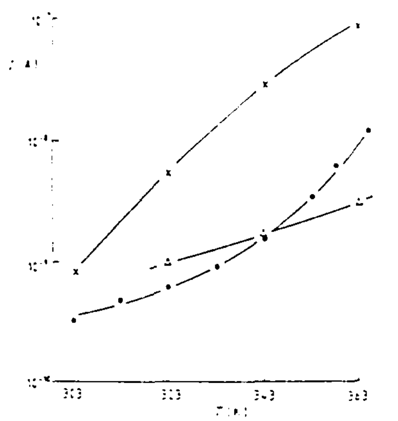

Figure 3 Isochronal charging currents at 10^4 sec in PZT PVDF and piezel at different temperatures and poling field $3.5 \times 10^6\,\mathrm{V\,m^{-1}}$. (×) PZT (50 vol%) PVDF, (●) piezel, (△) PZT (10 vol%) PVDF

which moves to shorter times at higher fields, may be due to space charges in PVDF [5]. Typical sets of charging and discharging currents in the composite are shown in Fig. 2 at the charging field of $7 \times 10^6\,\mathrm{V\,m^{-1}}$ at 363 K for 10 and 50 vol% PZT. The polarity of the discharging currents has been reversed for clarity. For discharging currents, the variation of the slope is very small, i.e. between 0.92 and 0.89 for changes in PZT composition.

The behaviour of isochronal charging currents (i.e. the current at constant times) at 10^2 sec at field of $3.5 \times 10^6\,\mathrm{V\,m^{-1}}$ in the composite is shown as a function of temperature in Fig. 3. The corresponding behaviour of piezel is also plotted for comparison. In all cases, the current increases with temperature although the nature of the increase is different in the three cases. At low temperature, the difference in current is very small but as the temperature reaches 363 K, a difference of about a factor of ~ 30 is found in PZT PVDF composites with 10 and 50 vol% PZT, again indicating the significant contribution of the PZT phase at high temperatures.

Fig. 4 indicates the behaviour of the isochronal charging current plotted as a function of field for PZT, PZT PVDF and piezel. Using the expression for a steady state current, I_s, as derived by Mott and Gurney [6]

$$I_s = I_0 \exp(-\mu/kT)\exp(edE/2kT) \qquad (1)$$

(where I_0 is a constant, μ the activation energy, d the jump distance, and the other symbols have their usual meanings), the jump distance for PZT is found to be ~ 90 nm, whereas for piezel, d = 28 nm and for PZT (50 vol%) PVDF, d = 8 nm. It may be observed that except for the PZT curve, the values of the charging current at 10^4 sec are not the steady state current for the other curves and hence the calculation of d-values for these curves may not be appropriate for comparison with PZT curves. Indeed, the values of d for piezel, calculated from steady state currents is greater, i.e. ~ 45 nm, hence the d-values for the PZT PVDF composite are expected to be greater than the values calculated at 10^4 sec. Comparing the PZT PVDF curves at 10 and 50 vol% PZT shows the addition of more PZT phase will increase the d-values.

Fig. 5 shows the behaviour of permittivity, ε' and ε'' with frequency for PZT PVDF composites and piezel at 363 K. The ε'-values for PZT (50 vol%) PVDF and piezel have been divided by 10, for the purpose of clarity. It may be observed that the ε' values for PZT PVDF tend to increase at lower frequencies and relax at frequencies higher than 10 kHz, while for piezel the variation in ε' values are not as much as that of PZT PVDF composites. According to Yamada *et al.* [7], the permittivity for the composite system is given as:

$$\varepsilon = \varepsilon_1\left[1 + \frac{nq(\varepsilon_2 - \varepsilon_1)}{n\varepsilon_1 + (\varepsilon_2 - \varepsilon_1)(1 - q)}\right] \qquad (2)$$

where n is the parameter attributed to the shape of the ellipsoidal particles, q the volume fraction of the ellipsoidal particles, ε_1 the permittivity of the continuous medium and ε_2 the permittivity of the ellipsoidal particles. Taking the values of ε_1 = 11 (PVDF), ε_2 = 1240 (PZT) and the value of n, chosen as 8 to fit Equation 2, the calculated values of relative permittivity at 1 kHz are ε' = 20 (for 10 vol% PZT) and ε' = 90 (for 50 vol% PZT) which are in good agreement with the observed values (see Fig. 5).

The dielectric loss behaviour (Fig. 5) of the PZT PVDF and piezel composites show relaxation with a broad peak which may be due to the relaxation of the polymer PVDF which occurs at a similar frequency and temperature range. The loss is seen to increase considerably at low frequencies for higher content of PZT in PZT PVDF, indicating the dominance of PZT at low frequencies.

Fig. 6 shows the dielectric loss behaviour against temperature in the composite of PZT/PVDF and piezel. The observed peaks which occur at ~ 360 K in

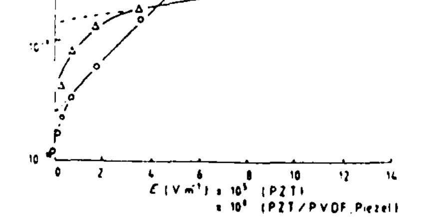

Figure 4 Isochronal charging currents at 10^4 sec as a function of field in PZT, PZT PVDF and piezel at 343 K. (×) PZT, (●) PZT (50 vol%) PVDF, (O) piezel, (△) PZT (10 vol%) PVDF

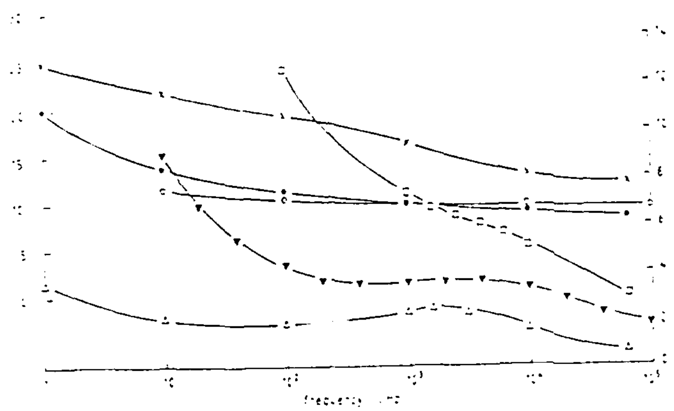

Figure 5 The behaviour of ε′ and ε″ against frequency in PZT PVDF and piezel at 3?? K. PZT (10 vol %) PVDF ... PZT (50 vol %) PVDF (●) ... (▼)

PZT PVDF and at ~ 350 K in piezel are due to relaxation which is associated with molecular motions in the crystalline region of the polymer. The observed values of ε″ also demonstrate the substantial contribution of the high PZT phase content of PZT PVDF composites at high temperatures.

A typical pattern of thermally stimulated currents run in PZT PVDF with 50 vol % PZT is shown in Fig. 7. The sample was poled in air at a field of 1.2×10^7 V m^{-1} and a temperature of 373 K for 2.5 h, and then cooled to room temperature under the field. It was then placed in a vacuum measurement chamber for thermally stimulated current measurement. With the sample short circuited, a linear heating rate of 1 K min^{-1} was applied from ~ 290 to 373 K and then cooled to room temperature. The first run shows a very high increase in current with no peak up to 373 K. From the shape of the curve, it may be possible to observe the peak if it is heated slightly above 373 K. A similar observation had been made by Shakhtakhtinski *et al.* [5] in which no peak had been observed below 373 K for a composite of PZT polyethylene. The second heating shows a substantial reduction of current as some charges have been released during the first heating. The third subsequent heating shows no appreciable current reduction, thus a reversible pyroelectric current is established. The pyroelectric coefficient $p(T)$ can be evaluated using the relation:

$$I_p = ap(T)\frac{dT}{dt} \qquad (3)$$

where I_p is the short-circuit pyroelectric current, a the sample area and dT/dt is the rate of change of temperature (°C sec^{-1}). Fig. 8 shows the calculated pyroelectric coefficients as a function of temperature for 10 and 50 vol % PZT of PZT PVDF composites which were obtained from the reversible thermally stimulated current data. It may be observed that the value of p for PZT (50 vol %) PVDF is ~ 4.5×10^{-4} C m^{-2} K^{-1} which is about 35 times higher than that of PZT (10 vol %) PVDF and significantly higher than that of well poled PVDF (~ 8×10^{-5} C m^{-2} K^{-1}) at the same temperature of 323 K.

In conclusion, it may be suggested that the electrical conduction behaviour in the PZT polymer composite may originate from an ionic hopping mechanism with a significant contribution from the PZT phase. However, the dielectric loss process has been controlled by

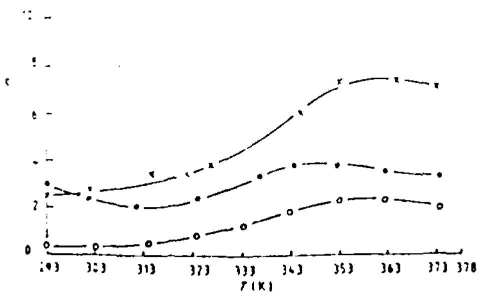

Figure 6 Dielectric loss behaviour against temperature in PZT PVDF and piezel at 1 kHz. (×) PZT (50 vol %) PVDF, (●) piezel, (○) PZT (10 vol %) PVDF

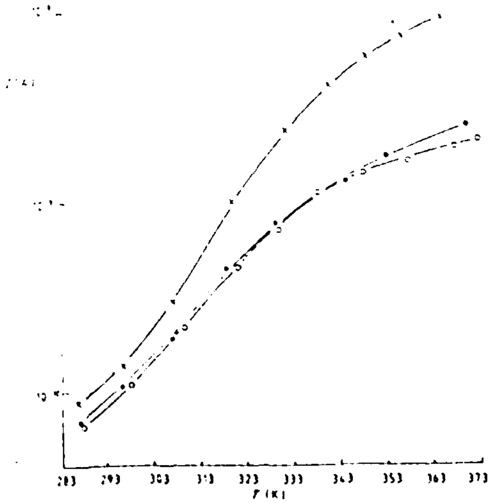

Figure 7 Thermally stimulated current in PZT (50 vol %) PVDF. E_p 1.2×10^7 V m^{-1}, T_p 373 K, t_p 2.8 h. Run (×) 1, (●) 2, (○) 3.

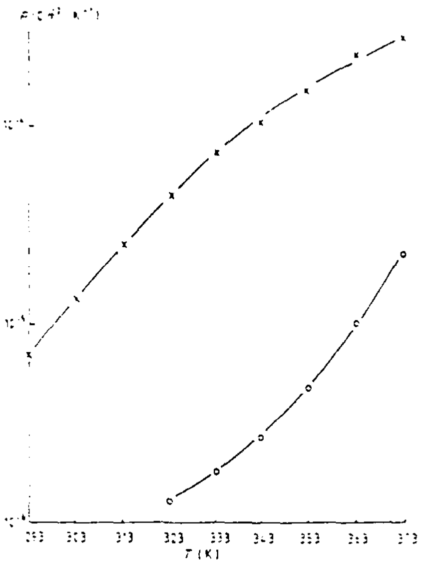

Figure 5 Pyroelectric coefficient of PZT/PVDF at different temperatures. E_p: 7×10^6 Vm^{-1}, T_p: 373 K, t_p: 2.5 h. (×) PZT (50 vol%) PVDF, (○) PZT (10 vol%) PVDF.

the polymer phase with some substantial contribution from the PZT phase at low frequency and high temperature regions. A significantly high pyroelectric coefficient and dielectric permittivity have been achieved in PZT (50 vol%) PVDF composite as compared to the single phase polymer.

Acknowledgements

This work was financed by a research contract from the European Research Office of the US Army. One of the authors (MJA) is grateful to the Malaysian Government for a maintenance grant.

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ELECTROACTIVE PROPERTIES OF POLYMER–CERAMIC COMPOSITES

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The nature of absorption and steady state electrical conduction as well as the dielectric and pyroelectric behaviour have been studied for polymer/ceramic composites. Experimentally observed values of pyroelectric coefficient and dielectric permittivity for various PZT content of PZT/PVDF composites seem to agree well with the calculated values. A high dielectric permittivity of polymer coupled with high pyroelectric activity of PZT may contribute to the high pyroelectric coefficient in the PZT/PVDF composites. The dielectric loss processes of the polymer ceramic composites are observed to be dominated by those of the polymer whereas the ceramic phase may contribute significantly to the steady state electrical conduction which is suggested to be of ionic origin.

1. INTRODUCTION

The use of ferroelectric devices based on titanate and niobate ceramic materials are expanding and is expected to give a greater impact in electronics industry in the future. However, their use in some engineering applications may be restricted due to its poor mechanical strength and inflexibility. Ferroelectric polymer materials such as polyvinylidene fluoride (PVDF) and its copolymer such as vinylidene trifluoride/vinylidene fluoride and vinylidene fluoride/trifluoroethylene have recently been employed for medical and industrial transducer applications. Relative to ceramics, they are flexible, tough, light and provide a good acoustic matching to water and biological tissue. Furthermore, thin films of these polymers can be cut or bent into complex shapes, which could provide an added advantage as compared to ferroelectric ceramics, although their piezo-and pyrolectric coefficient are relatively lower.

In recent times, ferroelectric composites of ceramic and polymer have received considerable attention due to their good piezoelectric properties for transducer applications.[1,2] There are many ways in producing polymer-ceramic composites,[3] but the simplest method is by introducing the ceramic particles into the polymer matrix. The polymer-ceramic composites thus constitute a new structure which might differ in many respects from their single phase components. Hence the design of the composites with optimum properties becomes very challenging since its properties do not only depend on the materials and the compositions but also on their interconnections. Such composites would exhibit piezo- and pyroelectricity if they are suitably poled.[4,5] The piezoelectric constant for the composite depends on the piezoelectric constant of the dispersoid, the dielectric permittivity and the elastic constant of both the phases.

Similar dependency may also be observed for the pyroelectricity of the composite. A detailed investigation is still needed to develop the material with optimum practical values for various applications.

Composite of PZT/PVDF have been prepared in our laboratories and the nature of their absorption currents have already been reported.[13] Present work reports the results of absorption current studies of a commercially available composite of a PZT/copolymer VDF (PIEZEL) together with quasi-steady state conduction, dielectric and pyroelectric behaviour of PZT/PVDF composite and PIEZEL. Some limited results of steady state conduction and dielectric studies of PZT has also been provided.

2. EXPERIMENTAL

PZT/PVDF composites are prepared from PZT5 ceramic powder (supplied by Unilator, U.K.) mixed up with PVDF pellets (grade Solef 11010, obtained from Laporte Trad., U.K.) at 443K using a hot roller machine and then pressing into film of approximately 200 μm in a temperature controlled hydraulic press. After depositing an aluminium electrode of area 2 cm × 2 cm and thickness 700 Å on both sides of the sample film, they were then thermally treated in an evacuated ($<10^{-5}$ torr) measurement chamber at 373K for 24 hours with their electrodes shorted before any application of external polarizing electric fields. Such thermal treatment prior to measurements was found to improve repeatability of the results and tends to reduce any trapped (shallow) charges and surface charges. Similar procedure of electrode depositing and subsequent thermal treatment of the samples were also performed for PIEZEL (nominal thickness of 250 μm, supplied by Daikin Industries Limited of Japan) and PZT (2 mm thickness, supplied by Unilator, U.K.).

A Brandenburg type 472R high stability photomultiplier EHT supply was used for charging or poling the samples. In the charging and discharging procedure, the samples were thermally conditioned as described earlier, before the application of each of the next charging fields. The currents were monitored with a Cary electrometer (model 401) or Keithley (model 602) which were then suitably fed to a recorder.

The dielectric data were taken using a General Radio Bridge (type 1621 with a 1238 detector and a 1316 oscillator) or using a Solartron Frequency Response Analyser and BBC microcomputer automatic system which have recently been developed at UCNW, Bangor. The pyroelectric currents were measured using a direct method,[6] in which a linear heating rate of approximately 1 deg/min was applied to the samples which have been poled appropriately. The pyroelectric responses of the sample were also studied by a dynamic method[7,8] by exposing the samples to a step input of well focused radiations from a tungsten filament lamp through a quartz window of the sample chamber.

3. RESULTS AND DISCUSSIONS

The effect of polarising fields at constant temperature on charging and discharging currents in PIEZEL is shown in Figure 1. The polarity of the discharging current

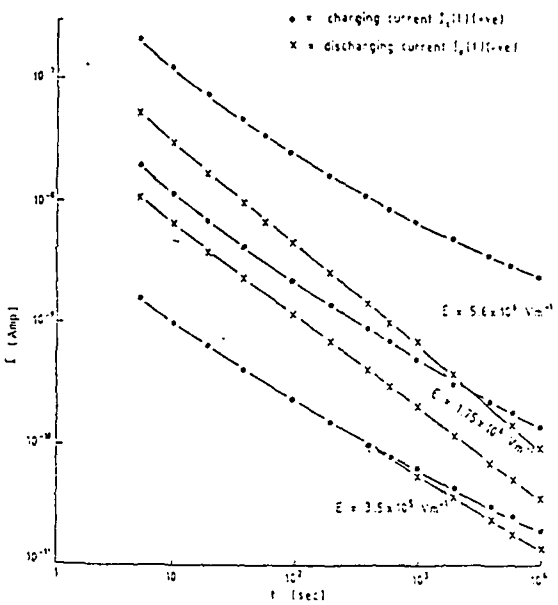

FIGURE 1 Charging and discharging currents in PIEZEL at different fields and temperature 313 K.

$I_d(t)$ has been reversed for the purpose of clarity. It may be observed that the difference in magnitude between $I_c(t)$ and $I_d(t)$ at constant times increased with increasing charging fields, demonstrating the influence of contributions of the steady state of conduction current at progressively shorter times. The behaviour of $I_c(t)$ and $I_d(t)$ at different temperatures in the range of 313 K–373 K at a charging field of $3.5 \times 10^{-5}\ \mathrm{Vm}^{-1}$ is shown in Figure 2. It may be observed again that at higher temperatures a steady state conduction begins to occur which causes the charging currents to deviate from the corresponding discharging currents at progressively shorter times with increasing temperatures.

Above observations are in agreement with the behaviour of $I_c(t)$ and $I_d(t)$ in polyvinylidene fluoride. The monotonic decay of the discharging currents with time were observed to follow the well known expression:

$$I(t) = A(T)t^{-n} \tag{1}$$

where $A(T)$ is a temperature dependent factor, t is the time after removal of the external applied field and $n < 1$ in the range of fields and temperatures of the present measurement. The steady state conduction currents were observed to have been reached at $\sim 10^{4.5}$ sec ($\simeq 27.8$ hours) at 293 K and $3.5 \times 10^5\ \mathrm{Vm}^{-1}$.

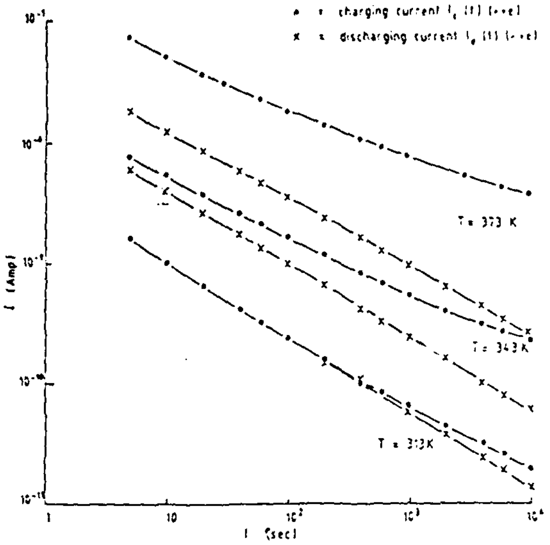

FIGURE 2 Charging and discharging currents in PIEZEL at different temperature and field $3.5 \times 10^5\ \mathrm{Vm}^{-1}$.

Obviously, at high fields and temperatures, the steady state conduction level is reached at relatively shorter times.

The conductivity of the PIEZEL sample at 343 K was observed to be $1.2 \times 10^{-12}\ \Omega^{-1}\ \mathrm{m}^{-1}$ which is about one order of magnitude higher than that of PVDF. It has been shown previously[9] that the charging currents in PZT reaches a steady state value at relatively shorter times (~100 sec) giving the conductivity value of $9 \times 10^{-10}\ \Omega^{-1}\ \mathrm{m}^{-1}$ at 343 K, which is about 3 orders of magnitude higher than that of PIEZEL. Thus the charging and discharging currents behaviour and the level of steady state conduction in PIEZEL are very close to that of polymer phase.

Figure 3 shows the nature of isochronal (i.e. at constant times) charging currents for different fields at a constant temperature of 343 K. An analysis of their behaviour shows that the slopes of log $I_c(t)$/log E plot at high fields region are greater than one and non-linear at longer times and higher fields, thus indicating possibly a presence of ionic or electronic space charges.

The temperature dependence of the steady state conduction I_s at 10^5 sec for different fields in PIEZEL is shown in Figure 4.

The behaviour of I_s as a function of field may be analysed with respect to three conduction mechanisms, i.e., Schottky emission, Poole–Frenkel effect and ionic conductivity. Previous results[10] have shown that the Schottky and Poole–Frenkel models many not be the origin of the steady state conduction current in PIEZEL.

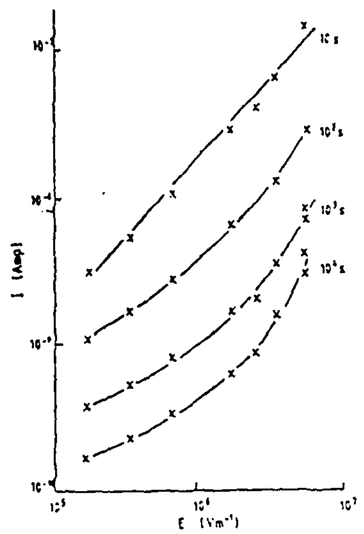

FIGURE 3 Isochronal charging currents in PIEZEL at different fields and temperature 343 K.

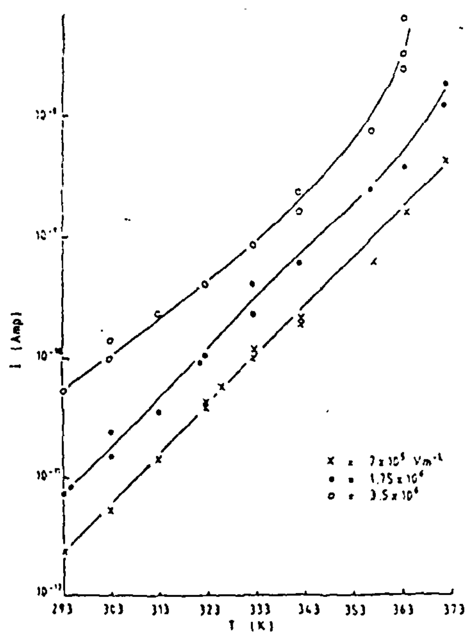

FIGURE 4 *Temperature dependence of quasi-steady state currents in PIEZEL at* 10^4 sec for different charging fields.

Das-Gupta *et al.*[11] have also rejected the possibility of Schottky and Poole–Frenkel conduction in PVDF.

Ionic conductivity has been observed unambiguously both in ceramic and polymeric systems. Based on a model of diffusion of lattice defects or ions and a carrier hopping process,[12] it may be shown that:

$$I_s = I_0 \exp(-\Delta U/kT)\,\mathrm{Sinh}(edE/2kT) \tag{2}$$

where I_0 is a constant, d the jump distance, ΔU the activation energy and E the applied electric field. Equation (2) may be reduced to:

$$I_s = I_0 \exp(-\Delta U/KT)\exp(edE/2kT) \tag{3}$$

for high electric field region ($eEd \gg 2kT$). Hence a plot of log I_s versus E at any particular temperature T should give a straight line at high fields with a slope of $edE/2kT$, from which the value of d may be evaluated. Figure 5 shows such an ionic plot in PIEZEL at several temperatures, giving the values of d in the range 450–850° A in the temperature range of 303–373 K. The values of d for PZT were found to be in the range 660–1020 A at temperatures 303–343 K while for PVDF[11], the average jump distance d was found to be (25 ± 5)A. Thus the ionic

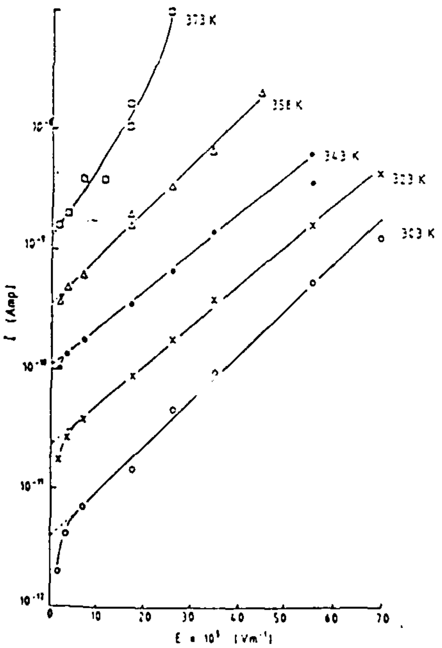

FIGURE 5 Ionic conduction plots in PIEZEL at different temperatures.

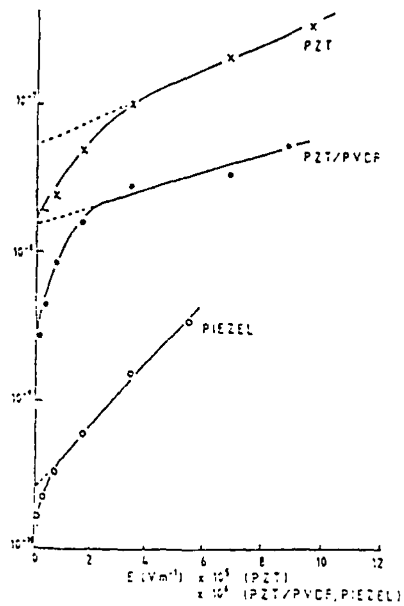

FIGURE 6 Isochronal charging currents at 10^4 sec as a function of field in PZT, PZT/PVDF and PIEZEL at 343 K.

conduction process in PIEZEL appear to have a significant contribution from the PZT phase.

The ionic plot for isochronal charging currents at 10^4 sec at 343 K in PZT, PZT (50 Vo. %)/PVDF and PIEZEL are shown in Figure 6 for comparison. The jump distance for PZT is found to be ~900 A, whereas for PIEZEL, $d = 280$ A and PZT/PVDF having $d = 80$ A. It should be noted, however, that except for the PZT curve, the values of charging currents at 10^4 sec are not the steady state current for the other two materials and hence the calculation of d-values for these materials may not be appropriate for comparison with PZT. The values of d for PIEZEL, calculated from steady state currents (~10^5 sec) is greater (~450 A); hence the d-values for PZT/PVDF composite is expected to be greater than the values calculated at 10^4 sec. The high d values obtained in PIEZEL, as compared to PZT/PVDF composite may be due to high content of PZT phase present in PIEZEL. Indeed, the increase of PZT phase content in the composite would increase the values of the jump distance.[13]

Figure 7 shows the behaviour of dielectric permittivity and loss in PIEZEL at different temperatures. It may be observed that the values of ϵ' decrease while its relaxation strength increases as temperature is increased in the range 324 K–375 K, thus indicating a thermally activated process. Such a process is clearly seen

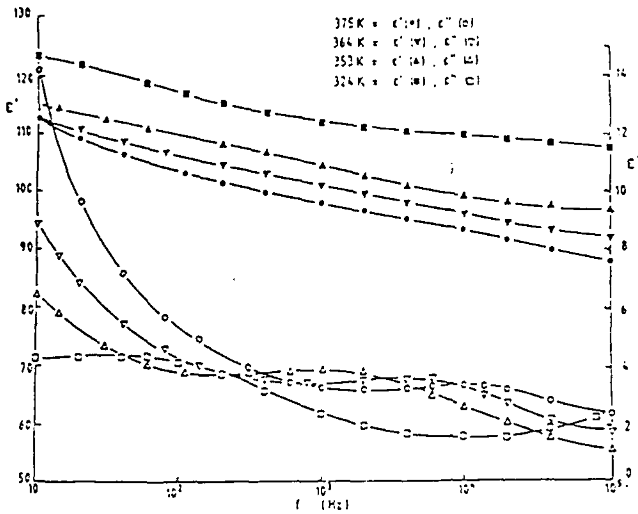

FIGURE 7 The behaviour of ϵ' and ϵ'' against frequency in PIEZEL at different temperatures.

in the behaviour of the loss function ϵ'' in which a broad relaxation peak is observed and it shifts to higher frequency for increasing temperatures. The activation energy of this process is found to be 1.20 eV which is comparable to that in PVDF, i.e. 1.0 eV[14]. This will suggest that the relaxation process in PIEZEL may be due to α_c-relaxation in the polymer phase, which has been assigned to molecular motions in the crysalline phase. Previous results[10] have also shown a presence of a low frequency ($\sim 10^{-5}$ H$_z$) peak in PIEZEL which corresponds well to that of polymer PVDF,[12] thus suggesting again that the dielectric behaviour of the composite is in good agreement with that of the polymer.

There is no observable relaxation process in PZT in the specified frequency range as can be seen from Figure 8, which suggests that there is no appreciable movement of domain walls or phase boundary. It may also be observed that a broad relaxation peak is also present in PZT/PVDF composite as shown in Figure 8. The high conductivity term of ceramic phase is seen to contribute significantly at low frequencies in the PZT/PVDF composite. The values of ϵ' for PIEZEL and PZT/PVDF appear to be the same at high frequencies, but it differs significantly at lower frequencies, which may be due to the interfacial charges residing in between particles of ceramic in the amorphous phase of the polymer. There is no appreciable change in the values of ϵ' for PZT in the frequency range of 10 Hz–100 kHz. Thus the high relaxation strength obtained in PIEZEL and PZT/PVDF composites may be due to the effect of ceramic particles in the amorphous phase of the polymer.

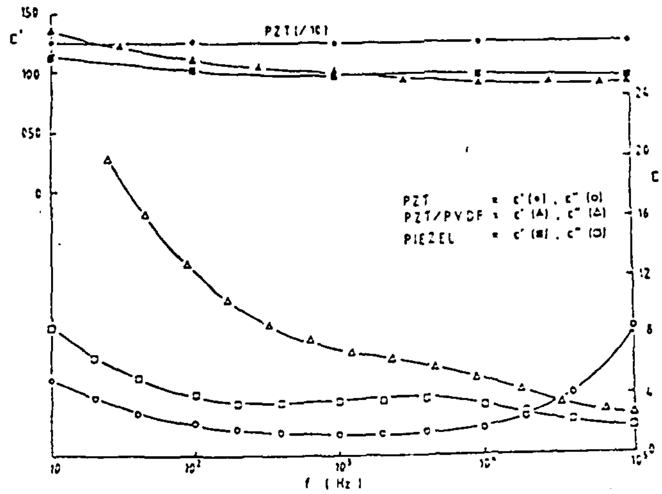

FIGURE 8 The behaviour of ε' and ε against frequency in PZT, PZT/PVDF and PIEZEL at 363 K.

The dielectric loss behaviour with temperatures in PZT, PIEZEL and PZT/PVDF composite are shown in Figure 9, from which it may be observed that there is a relaxation peak in both composites of PIEZEL and PZT/PVDF while in PZT there appears to be no relaxation. The relative difference of peak position may be attributed to the nature of polymers employed. Again, the loss process seemed to be due to polymer phase with an added contribution from PZT phase at low frequencies and high temperatures.[13]

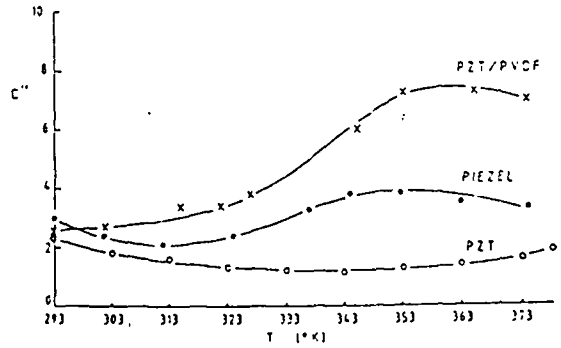

FIGURE 9 Dielectric loss behaviour against temperature in PZT, PZT/PVDF and PIEZEL at 1 kHz.

Assuming a composite system in which ellipsoidal particles (ceramic) are uniformly distributed in a continuous medium (polymer), the dielectric permittivity ϵ of the system is expressed as:[4]

$$\epsilon = \epsilon_1 \left\{ 1 + \frac{nq(\epsilon_2 - \epsilon_1)}{n\epsilon_1 + (\epsilon_2 - \epsilon_1)(1 - q)} \right\} \tag{4}$$

where $n = 4\pi/m$ is the parameter attributed to the shape of the ellipsoidal particles, q is the volume fraction of the ellipsoidal particles, ϵ_1 is the permittivity of the continuous medium and ϵ_2 the permittivity of the ellipsoidal particles. Using $\epsilon_1(\mathrm{PVDF}) = 11$, ϵ_2 (PZT) = 1300 at 363 K, the calculated values of permittivities with $n = 7$ and 8 are plotted as a function of PZT volume percentage, along with the experimentally observed values, in Figure 10. The theoretical curve with n value being between 7 and 8, may reasonably fit the experimental data obtained, which is in good agreement with the curve obtained by Yamada *et al.* [4] in PZT/PVDF ($n = 8.5$) and Muralidhar and Pillai[15] in $BaTiO_3$/PVDF ($n = 7$). It may also be observed from Figure 10 that the dielectric loss is inevitably increased as the PZT content is increased, and it is markedly observed particularly in the low frequency region.

In the direct method[6] of measuring pyroelectric coefficient a sample is heated at a constant rate with its electrodes shorted and the short-circuit current is monitored with an appropriate impedance electrometer. The first run provides irreversible current which is subsequently reduced in the following runs. A typical thermally stimulated discharge current (irreversible) and pyroelectric current (reversible) in PZT (50 vol %)/PVDF is shown in Figure 11 which was obtained with the pre-poled sample at 373 K in electric field of $1.2 \times 10^7\ \mathrm{Vm^{-1}}$ for 2.8 hours and cooled to room temperature in the presence of field. The first run shows a very high increase in current with no peak up to 373 K. It may be

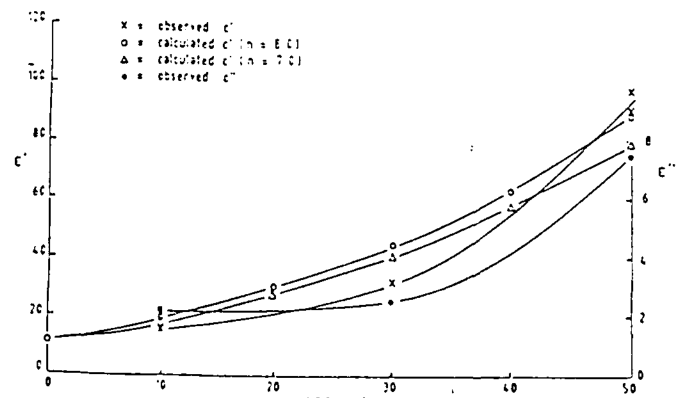

FIGURE 10 Dielectric permittivity and loss as a function of ceramic volume percentage in PZT/PVDF composite at 1 kHz and 363 K.

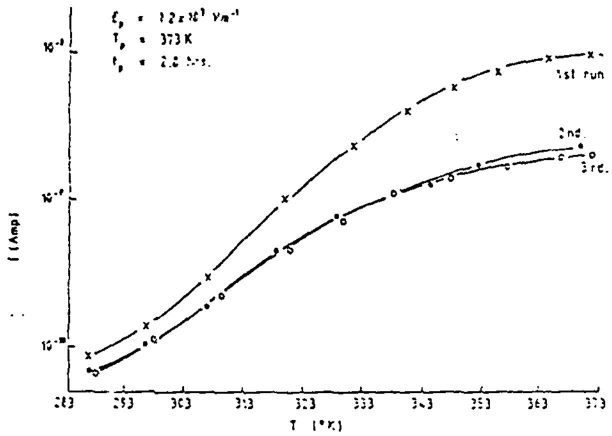

FIGURE 11 Typical thermally stimulated discharge current and pyroelectric current in PZT/PVDF composite.

possible to observe the peak if it is heated slightly above 373 K. Similar observation had been made by Shalchtalchtinskii *et al.*[16] in which no peak had been observed below 373 K for composite of PZT/polyethylene. The second heating shows substantial reduction of current as some charges have been released during the first heating. The third subsequent heating shows no appreciable current reduction, thus establishing a reversible pyroelectric current in the sample. The pyroelectric coefficient $p(T)$ can be evaluated using the following relation:

$$P(T) = \frac{1}{a}\left(\frac{I_p}{dT/dt}\right) \tag{5}$$

where I_p is the short-circuit pyroelectric current, a the sample area and dT/dt is the heating rate (1 deg/min). The calculated value of $p(T)$ at 343 K gives about 2×10^{-4} coul/m^2/K which is significantly higher than that of the well poled β-PVDF ($\cong 1 \times 10^{-5}$ Coul/m~/K) obtained by Inoue *et al.*,[17] at the same temperature. Although the p value in PZT/PVDF composite is lower than that of PZT ($p \approx 5 \times 10^{-4}$ Coul/m~/K), its pyroelectric figure of merit p/ϵ' is about 5 times higher (taking ϵ'(PZT/PVDF) $\approx$ 95, $\epsilon'(PZT) = 1250$ at 343 K).

Figure 12 shows the behaviour of the first run (irreversible pyroelectric current) and the third run (reversible pyroelectric current) of the TSDC spectra for different PZT content of PZT/PVDF composites. It may be observed that the differences between the current values of these two runs is more pronounced for low concentration of the ceramic in the polymer matrix. A possible explanation for this behaviour may be described as follows. The conductivity σ of an ionic

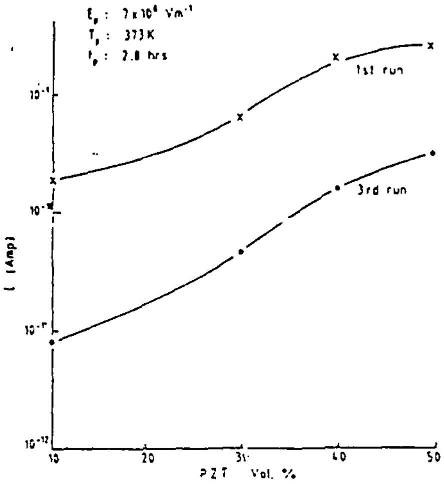

FIGURE 12 Thermally stimulated discharge currents spectra for various ceramic volume percentage at 323 K in PZT/PVDF composite.

material may be expressed as:

$$\sigma^{*} \exp - \left[\frac{\Delta W}{\epsilon' KT}\right] \tag{6}$$

where the activation energy U is given by $\Delta U = \Delta W/2\epsilon'$ and W is the energy required to separate the ions in a dielectric medium. Equation (6) implies that the conductivity is increased due to an increase in the permittivity ϵ'. Thus, a higher conductivity would arise for high PZT content of the composite. In addition it is possible that an increasing ceramic content may introduce deeper traps resulting in a decrease of released charges. Of course, it should be stated that an increase in conductivity does not necessarily provide an increase in the reversible pyroelectric current.

The pyroelectric coefficient for various contents of PZT in PZT/PVDF composite at three different temperatures are shown in Figure 13. The samples were initially poled using the same poling parameters. ($E_p = 7\times10^6$ x 1/m, $T_p = 373$ K, $tp = 2.8$ hrs). Generally, the pyroelectric coefficient increases as the PZT content in the composite increases. Assuming that the pyroelectric coefficient for the composite depended on the pyroelectric coefficient of the dispersoid and the relative permittivity of the polymer, the composite pyroelectric coefficient p may be expressed as.[4,5]

$$P = q\alpha GP_2 \tag{7}$$

where q is the dispersoid volume fraction, α the poling ratio which is defined as the ratio of an arbitrary chosen value of polarization to the saturation value at a

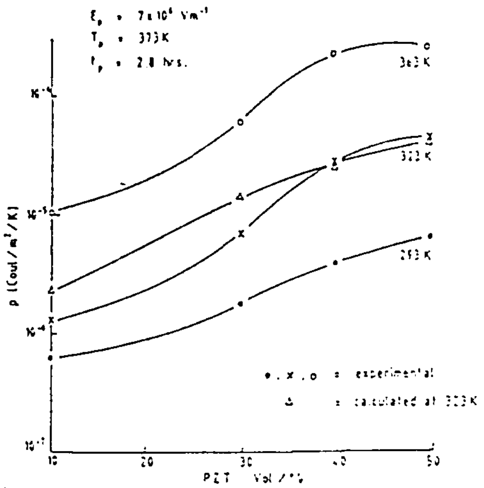

FIGURE 13 Pyroelectric coefficient at different temperatures as a function of ceramic volume percentage in PZT/PVDF composite.

particular field, p_2 pyroelectric coefficient of the dispersoid and G is the local field coefficient given as:

$$G = \frac{n\{\epsilon_2/\epsilon_1 - 1 + n + (n-1)(\epsilon_2/\epsilon_1 - 1)q\}}{(\epsilon_2/\epsilon_1 - 1 + n)^2 + (\epsilon_2/\epsilon_1 - 1)\{(n-1)^2 - \epsilon_2/\epsilon_1\}q} \tag{8}$$

where the symbols have been previously defined. Using $n = 7.5$, $\alpha = 0.8$, $\epsilon_1 = 11$, $\epsilon_2 = 1200$ and $p_2 = 3 \times 10^{-4}$ Coul/m~/K, the calculated values of p are obtained for PZT/PVDF composites with different PZT content at 323 K, and are shown in Figure 13. It may be observed that there is a good agreement between experimental data and calculated values for composites with high content of PZT phase. For low PZT content, the observed values of the pyroelectric coefficients were less than the calculated values. This deviation may be caused by the uncertainties in the chosen values of α.

The dynamic method[7] provides an alternative way in measuring the pyroelectric response of the materials. The pyroelectric coefficient $p(T)$ in this method may be obtained from the following relation:

$$I_{p_{max}} = Kp(T) \tag{9}$$

with

$$K = \frac{F_o a}{\rho C_p L} \theta^{\theta \cdot 1 - \theta} \tag{10}$$

where Ip_{max} is the peak value of the pyroelectric current response, ρ material density, F_0 is the radiation power absorbed per unit area of the electroded

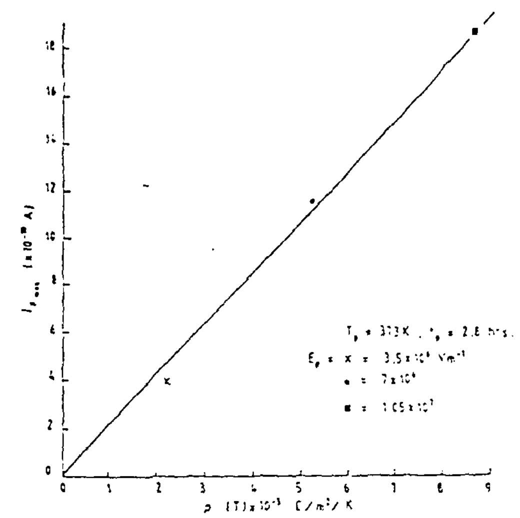

FIGURE 14 Peak current against pyroelectric coefficient at 333 K in PZT/PVDF composite.

sample, C_p the specific heat, L the sample thickness and $\theta = E/T$ where E and T are the electrical and thermal time constants of the system. $I_{p_{max}}$ was measured when a step input of radiation was incident onto the sample electrode after the completion of the third TSDC run of the pre-poled sample. Figure 14 shows that there exists a linear relationship between the pyroelectric coefficient $p(T)$ determined by the direct and the dynamic methods with composite samples poled at three different fields in the range $(3.5–10.5) \times 10^6\ \mathrm{Vm}^{-1}$.

The constant of proportionality K (see Equation (9)) is found to be $2.1 \times 10^5\ \mathrm{m^2\,s^{-1}\,K}$, which could be considered as a constant for the same sample material having the same electrode geometry with the incident radiation power and the electrical, the thermal time constants of the system remaining unchanged. A comparison of pyroelectric coefficient between PZT/PVDF composite and PIEZEL, obtained by the direct method can be seen in Figure 15. Both composites show an appreciable increase of $p(T)$ values with temperatures. The value of $p(T)$ may still be enhanced by increasing the magnitude of poling field, limited by the breakdown voltage of the material. It may also be observed from Figure 15 that the $p(T)$ values obtained by the direct method in PZT/PVDF composite which is indeed the most accurate method, are somewhat higher than those obtained by the dynamic method, particularly at high temperatures. Further work is necessary in this respect.

In conclusion, it is suggested that the steady state conduction process in the polymer-ceramic composites may originate from an ionic hopping mechanism which has a significant contribution from the PZT phase. The dielectric loss

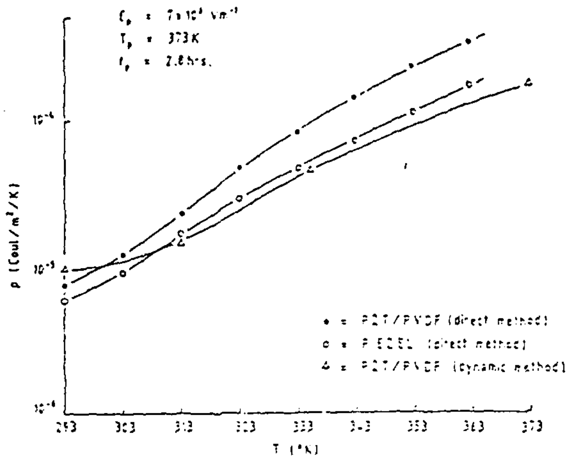

FIGURE 15 Pyroelectric coefficient against temperature in PZT/PVDF and PIEZEL.

processes are essentially due to the polymer phase with an added contribution by the PZT phase particularly at low frequencies and high temperatures. The dielectric constants and the pyroelectric coefficients appear to have a reasonably good agreement between the calculated and the experimentally observed values. A significantly high pyroelectric figure of merit has been achieved in high PZT content of PZT/PVDF composite as compared to that of PZT.

ACKNOWLEDGEMENT

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PYROELECTRIC AND DIELECTRIC PROPERTIES OF POLYMER-CERAMIC COMPOSITES

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INTRODUCTION

Ferroelectricity in well-poled polyvinylidene fluoride (PVDF) is a phenomenon which is now well supported. However, the piezo- and pyroelectric responses in this polymer are significantly weaker than those of ceramic oxides. It would be attractive to design composite materials which will have the mechanical properties of polymers with the electro-active properties of ceramics. Such materials will be useful for diverse sensor applications, viz, acoustic emission detection, hydrophones, biomedical applications, thin film capacitors etc. One of the chief requirements of a capacitor is that a large capacitance to volume ratio is desirable. A high ratio requires a thin film, a high dielectric constant and an acceptable electrical breakdown strength. Such a material may be designed by a judicious incorporation of fine grain ceramics in a suitable polymer matrix.

Present work reports the result of an investigation of the dielectric and pyroelectric properties of composite films in which $BaTiO_3$ and PZT have been located in the matrix of PVDF.

EXPERIMENTAL

PVDF pellets (types A and B) and fine grain (1-2μm) PZT5 and PZT8 were obtained from Laporte Industries and Unilator Technical Ceramics Limited., respectively. Cockson plc. generously provided us with $BaTiO_3$ grains (~1μm). The composite hides were prepared with suitable concentrations in a rolling mill at 433K. A temperature controlled hydraulic press was subsequently used in the second stage to prepare films of minimum thickness of 200μm. The absorption current studies, the dielectric measurements and pyroelectric behaviour investigations were made as described in our previous work[1-4]. The different composite mixtures used in this work will be designated thus:

Composite A: PZT5/PVDF-A (Solef 11010): 50/50 (volume fraction)

Composite B: PZT8/PVDF-B (Solef 1008): 50/50 (volume fraction)

Composite C: $BaTiO_3$/PVDF-B (Solef 1008): 40/60 (volume fraction)

PVDF-A pellets (Solef 11010) of Composite A films were observed to be more opaque compared to PVDF-B (Solef 1008) of Composite B films. Above observations would suggest that the Solef 11010 pellets are more crystalline in nature than the Solef 1008 PVDF pellets.

RESULTS AND DISCUSSION

Figure 1 shows typical charging and discharging current transients $I_c(t)$ and $I_d(t)$ respectively for the composite films A, B and C for a charging field of 3.5×10^5 Vm^{-1} at 363K. It may be observed that composite C reaches a quasi-steady state value of $I_c(t)$

at ~10^3s while composites A and B seem to take a longer time (~10^4s) to reach such conduction levels. It has been shown that the steady state conduction mechanisms[1] in such composites is of ionic nature which is also true for ceramic materials. Furthermore, ionic conduction has also been observed in PVDF at high fields and high temperatures where the charge carriers hop through the defect sites along the chains[5]. The discharge current $I_d(t)$, behaves according to the well known expression:

$$I_d(t) = A(T)\ t^{-n} \qquad \ldots (1)$$

where A(T) is a temperature dependent factor, t the time after the removal of the charging voltage and $n \leq 1$. In this work n-value was found to be 0.6 - 0.7 for all three composites. A very broad distribution of relaxation times is indicated by $n \simeq 1$.

The observed dielectric behaviour (ϵ' and ϵ'') of the three composites are given in figure 2 in the frequency range of 10 Hz - 65 kHz. For composites A and B the ϵ' - values (real part of the dielectric constant) are very similar and higher than that of composite C. The permittivity ϵ of a composite system may be expressed thus[6]:

$$\epsilon = \epsilon_1 \left[1 + \frac{nq(\epsilon_2 - \epsilon_1)}{n\epsilon_1 + (\epsilon_2 - \epsilon_1)(1-q)} \right] \qquad \ldots (2)$$

where ϵ_1 is the permittivity of the continuous medium (i.e. PVDF in our case), ϵ_2 permittivity of the ellipsoidal particles (ceramics), n a parameter attributed to the shape of the ellipsoidal particles. With n = 8, ϵ_1(PVDF) = 12, ϵ_2(PZT) = 1300 and ϵ_2 ($BaTiO_3$) = 1700, the calculated values of permittivities of composites A and C are 96 and 70 respectively which are in good agreement with the experimentally observed values, i.e. $\epsilon'_{composite\ A} = 100$, $\epsilon'_{composite\ B} = 105$ and $\epsilon'_{composite\ C} = 80$ at 1kHz at 363K.

The ϵ'' behaviour shows a broad relaxation (noticeably more for Composite C) at ~1kHz which is attributed to α_c-relaxation of the polymer (PVDF) phase. For composites A and B, the ϵ'' values increase significantly as the frequency is reduced and this may be attributed to an ionic conductivity or electrode polarization effect. Composite C also shows such a behaviour as the frequency goes below 10 Hz.

The behaviour of ϵ'' at 1kHz in the temperature range of 293-378K is shown in figure 3.

The observed high temperature peak at ~363K is in agreement with that in PVDF and it is associated with molecular motions in the crystalline region of the polymer[4] with added contributions from the ceramic phase. The increased dielectric loss with increasing temperature is usually ascribed to the ionic conductivity which is present in both the polymer and the ceramic phases.

Thermally stimulated discharge current (TSDC) plots of the three composites which were initially poled at a field of 7×10^6 Vm^{-1} for ~3 hours at 373K and cooled down to room temperature in presence of this field, is shown in figure 4. The TSDC spectra of composites A and B are similar and have higher values of thermally stimulated currents than that of composite C.

The pyroelectric coefficient p may be expressed thus:

$$p = \frac{1}{a} \left[I_p \Big/ \frac{dT}{dt} \right] \qquad \ldots (3)$$

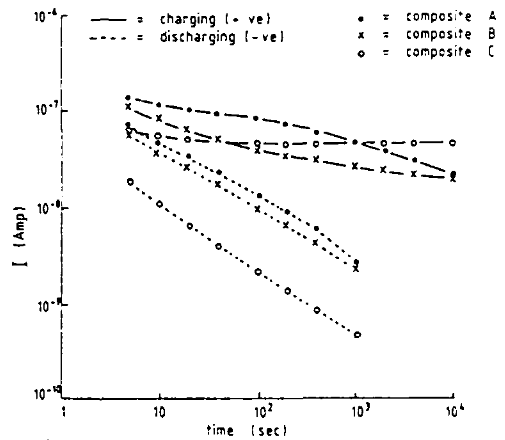

Figure 1: Charging and discharging currents in ceramic/polymer composites at 363 K and field 3.5×10^5 $V m^{-1}$.

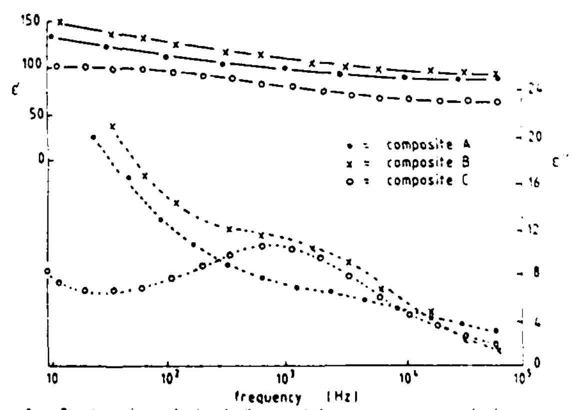

Figure 2: The behaviour of ε' and ε'' against frequency in ceramic/polymer composites at 363 K ε' = ——, ε'' = ----

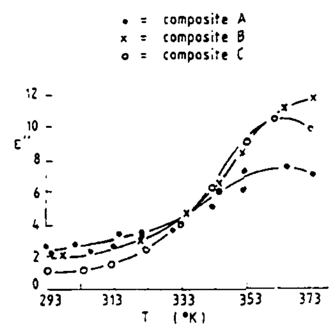

Figure 3 : Dielectric loss behaviour against temperature in ceramic/polymer composites at 1kHz.

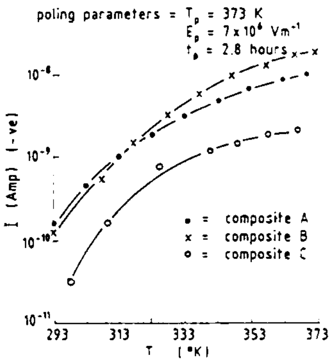

Figure 4 : Thermally stimulated discharge current in ceramic/polymer composites.

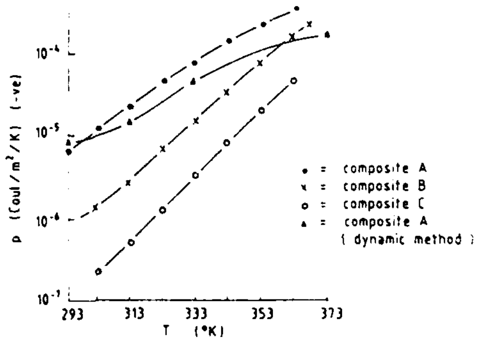

Figure 5 Pyroelectric coefficient against temperature in ceramic/polymer composites

where I_p is the reversible pyroelectric current and dT/dt is the rate of rise in temperature in a TSDC run. This is the direct method of determining pyroelectric coefficient. For our measurements I_p values were identified from the third successive run of TSDC experiment thus ensuring that the trapped space charges have been eliminated and that I_p is truly reversible. The heating rate in the present TSDC run is 1°c/min and a is the electrode area of the samples. Figure 5 shows the behaviour of the pyroelectric coefficient p with temperature in the range of 303K - 373K from which it may be observed that Composite A has the highest pyroelectric coefficient as compared with the other two composites. It may also be noticed that p values of Composite A is greater than that of Composite B by approximately an order of magnitude at 303K. It is suggested that the observed higher dielectric losses (see figure 2) coupled with its lower elastic stiffness in the polymer phase may be responsible for its smaller p-values compared with that of Composite A which would be in agreement with Galgoci et al[7]. Tamura et al[8] also have observed increased piezoelectric coefficient with increasing elastic stiffness. The pyroelectric figure of merit p/ϵ', in Composite A (1.5×10^{-6} $Cm^{-2}K^{-1}$) is approximately 3.8 times greater than that of PZT (3.8×10^{-7} $Cm^{-2}K^{-1}$) at 343K.

Pyroelectric coefficient has also been measured in this work by a dynamic method in which p(T) may be obtained from the following relationship[9].

$$I_{p(max)} = Kp(T) \qquad \ldots(4)$$

where

$$K = \frac{F_o a}{P c_p L}\, \theta^{\frac{\theta}{(1-\theta)}} \qquad \ldots(5)$$

where F_o is the radiation power absorbed per unit area of the electroded sample, a the electrode area, P the density of the material, C_p the specific heat, L the sample thickness, $I_{p(max)}$ the peak pyroelectric current response to a stepwise radiation incident on the sample, and $\theta = \tau_E/\tau_T$ where τ_E and τ_T are the electrical and thermal time constants of the system.

$I_{p(max)}$ was measured at different temperatures using a stepwise thermal radiation from a tungsten filament lamp. The pyroelectric coefficients p(T) were calculated using the measured values of $I_{p(max)}$ of the dynamic method and equations 4 and 5 for composite A and are also shown in Figure 5. It may be observed that the p(T) values obtained by the direct method which is indeed the most accurate method, are somewhat higher than those obtained by the dynamic method, particularly at high temperatures. Further work is in progress in the study of electro-active properties of Composite A which appears to be the most attractive material of the three Composites investigated in the present work. Table 1 provides a summary of results obtained in this work.

ACKNOWLEDGEMENT

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TABLE 1 - SUMMARY OF RESULTS

	$\sigma(\Omega^{-1}m^{-1})$ (90°C)	ϵ' (70°C) (1KHz)	ϵ'' (70°C) (1kHz)	Pyrelectric Coefficient p(T) (Coul.$m^{-2}K^{-1}$) (70°C)	Pyroelectric Figure of Merit p/ϵ'(70°C)
PZT	$3x10^{-9}$	1300	1.2	$5x10^{-4}$	$3.8x10^{-7}$
$BaTiO_3$	$10^{-9}-10^{-8}$	1700		$7x10^{-4}$	$4.1x10^{-7}$
PVDF	$3x10^{-13}$	12	1.0	$9.0x10^{-6}$	$7.5x10^{-7}$
Composite A [PZT5/PVDF(A)] 50:50	$1.4x10^{-10}$	95	6.0	$1.4x10^{-4}$	$1.5x10^{-6}$
Composite B [PZT8/PVDF(B)] 50:50	$1.3x10^{-10}$	96	6.5	$3.3x10^{-5}$	$3.4x10^{-7}$
Composite C [$BaTiO_3$/PVDF(B)] 40:60	$3x10^{-10}$	73	6.2	$8.0x10^{-6}$	$1.1x10^{-7}$

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310

Technical Information

Daikin Fluoro-Chemicals

APPENDIX

Piezoelectric Polymer Composite

Piezel

Introduction

Piezel is a flexible, piezoelectric polymer composite consisting of fine piezoelectric ceramics powder dispersed in fluoropolymers. This material makes it possible to obtain large-area, thin-film sheets, and to achieve mass production — both of which are impossible with piezoelectric ceramics.

Moreover, Piezel is superior to ordinary piezoelectric polymers with respect to processability and piezoelectricity, and there is no piezoelectric anisotropy.

Piezel is therefore a superior piezoelectric material which combines the merits of piezoelectric ceramics and polymers.

DAIKIN INDUSTRIES, LTD.

1. Grades

Piezel is available in the following two grades.

Product no.	Thickness T (mm)	Width W (mm)	Length L (mm)
N25	0.25	200	200
L25	0.25	200	200

In addition to these two grades, the following types can be specially ordered.
- P type (polarization treated)
- E type (polarization treated, with electrodes)

All grades can also be specially ordered with different dimensions.

2. Features

Piezel possesses many excellent features.
The main features are as follows.

2-1 Flexibility

Because Piezel uses fluoropolymers as a matrix, it is both flexible and superior in impact resistance to piezoelectric ceramics.

2-2 Excellent processability

Large-area sheets can be obtained, and processing, such as cutting, etc., is easily done. Moreover, Piezel also makes heat-processing possible.

2-3 Excellent piezoelectricity

A high degree of piezoelectricity can be achieved, and there is no piezoelectric anisotropy.

2-4 Long service life

Piezel displays almost no piezoelectric deterioration even after long use.

3. Properties

3-1 General properties

Item		N25	L25
Specific gravity		5.5 ~ 6.0	5.3 ~ 5.8
Elasticity E ($N/m \times 10^9$)		2 ~ 5	3 ~ 6
Tensile strength TS (kgf/cm^2)		150 ~ 200	150 ~ 200
Volume resistivity ρv ($\Omega \cdot cm$)		10[illegible]	10[illegible]
Dielectric constant ε (at 1 kHz)		100 ~ 120	120 ~ 180
Breakdown voltage BDV (MV/m)		8	8
Piezoelectric constant	d_{31} ($C/N \times 10^{-12}$)	15 ~ 25	20 ~ 30
	e_{31} ($C/m^2 \cdot 10^{-1}$)	0.5 ~ 1	1 ~ 5
	g_{31} ($Vm/N \cdot 10^{-3}$)	15 ~ 25	15 ~ 25
	k_{31} (%)	4.5 ~ 5.5	5.5 ~ 6.5
	d_{33} ($C/N \cdot 10^{-12}$)	40 ~ 60	30 ~ 40
	e_{33} ($C/m^2 \cdot 10^{-1}$)	1 ~ 2	1 ~ 2.5
	g_{33} ($Vm/N \cdot 10^{-3}$)	40 ~ 60	20 ~ 30
	k_{33} (%)	7 ~ 12	5 ~ 8

Note: Condition shown in 5-2. Measured at 25°C (77°F)

3-2 Temperature characteristics

Figures 1, 2, and 3 show the relationship between piezoelectric constant (d_{31}) and temperature; between modulus of elasticity (E) and temperature; between dielectric constant (ε) and temperature.

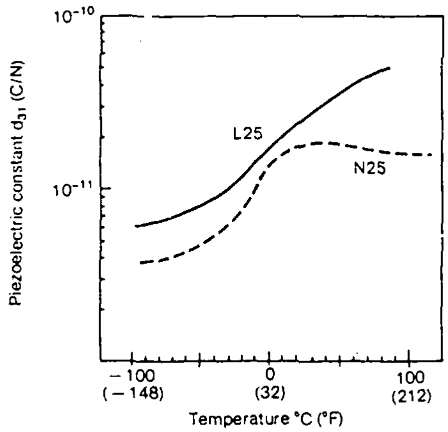

Figure 1 Piezoelectric Constant vs. Temperature

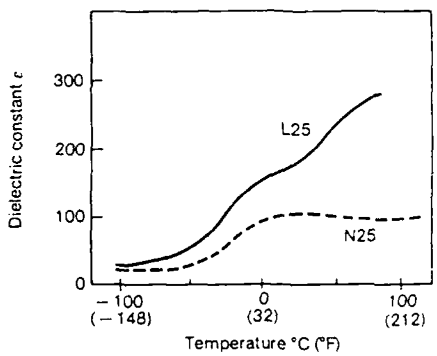

Figure 3 Dielectric Constant vs. Temperature

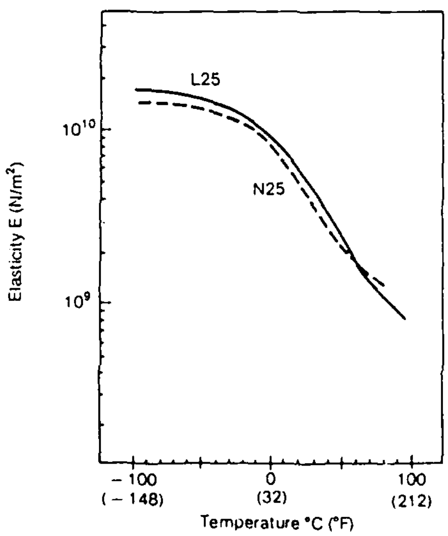

Figure 2 Elastic Modulus vs. Temperature